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WAVE MECHANICS
AND
THE NEW QUANTUM THEORY

INTRODUCTION TO
THEORETICAL PHYSICS

By ARTHUR HAAS, Ph.D.
Translated by T. VERSCHOYLE,
M.C., Ph.D., A.R.C.S.
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ATOMIC THEORY: AN
ELEMENTARY EXPOSITION

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WAVE MECHANICS AND THE NEW QUANTUM THEORY

BY

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AUTHOR OF

“INTRODUCTION TO THEORETICAL PHYSICS”

“ATOMIC THEORY,” ETC.

TRANSLATED FROM THE GERMAN EDITION
("MATERIEWELLEN UND QUANTENMECHANIK")

BY

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AUTHOR'S PREFACE

ALTHOUGH not much more than two years have elapsed since the foundation of Heisenberg's quantum mechanics, the planning of a book on this, the youngest branch of physical science, running into a thousand pages or more, seems possible. In the opinion of the author, however, besides such a complete and comprehensive work there should be some demand for a shorter treatise dealing with the subject from a broader standpoint, such as should appeal to the layman as well as to the professional physicist. A work of this kind should put forward the essential features of the ideas of de Broglie, Schrödinger and Heisenberg in a form that does not require an advanced knowledge of mathematics; should develop the close connection between these various ideas, and should demonstrate their significance by means of their most important applications. Such a treatment has been attempted in the present work, which is based upon lectures given by the author at the University of Vienna during the winter session 1927-28. As far as possible the most important advances in wave and quantum mechanics which have occurred since the appearance of the German edition (February, 1928) have been taken into account in the present English edition.

ARTHUR HAAS.

July, 1928

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SUMMARY OF CONTENTS

CHAPTER I.—Introductory remarks on the difference between the conceptions of mechanics and physics, the principles of the mechanics of relativity, the ideas of light quanta, gradation of energy in the atom and Bohr's principle of quantisation. The fundamental difficulties in Bohr's theory which require solution are : (1) the contradiction between the principles of classical mechanics as applied to the atomic model and the choosing of permissible orbits ; and (2) the determination of mechanical processes by the essentially optical constant \hbar .

CHAPTER II.—Fermat's principle, the fundamental theorem of geometrical optics, which states that the line integral of the reciprocal of the wave velocity is a minimum, exhibits a close relationship to the fundamental law of mechanics, Maupertuis' principle, which states that the line integral of the mechanical velocity is a minimum. This analogy justifies the expectation that the phenomena of motion may depend upon some kind of wave mechanism in which there is a universal proportionality between the mechanical velocity and the reciprocal of the wave velocity. Such an expectation is also supported by the connection to be found between the general wave formula and the Lorentz Transformation. If an undulatory process is imagined to be associated with a moving particle, application of the Lorentz Transformation leads to the result that this undulatory process must be regarded as a wave travelling with a velocity greater than that of light, whose group velocity corresponds with the mechanical velocity of the moving particle.

CHAPTER III.—De Broglie assigns an undulatory process to every moving particle by means of the formula :

$$mc^2 = \hbar\nu,$$

and thus obtains the laws of mechanics as a necessary consequence of a general wave principle. The electrons and protons therefore appear as energy centres in so-called material waves, whose wavelength is determined by the quotient of the elementary quantum of action and the momentum. When applied to uniform motion in a closed orbit, this hypothesis leads to the conclusion that only those orbits are possible for which the length of the orbit is an integral multiple of the wavelength, and for which, therefore, the angular momentum is an integral multiple of $\hbar/2\pi$. Transference of de Broglie's ideas to the case of a gas in a closed vessel leads, on the basis of characteristic vibrations, to a quantisation of the translational energy of the molecules, and a subdivision of the "momentum space" into cells equal in size to the quotient of \hbar^3 and the volume of the gas.

CHAPTER IV.—The relativity formula connecting the mass and the velocity, the formulæ for the longitudinal and transversal mass and the principle of the inertia of energy are derived from the assumption that material particles are the energy centres of waves, made up of energy elements $\hbar\nu$, whose group velocity is manifested as the mechanical velocity.

CHAPTER V.—The diffraction of material waves predicted by de Broglie's theory appears to be confirmed by observations on the scattering of electrons by gases, by the experiments of Davisson and Germer in the selective reflection of electrons by crystals and by the experiments of G. P. Thomson and Rupp on the passage of cathode rays through thin metal foil.

CHAPTER VI.—Following on the ideas of de Broglie, Schrödinger attempted a generalisation of mechanics

analogous to the transition from Fermat's to Huygens' principle, *i.e.*, from the geometrical optics of rays to the physical optics of waves. Application to an individual particle leads to the fundamental differential equation :

$$\Delta S + \frac{8\pi^2 m}{h^2} (E - V) S = 0,$$

where S is an undetermined field scalar, E is the total and V the potential energy. By this relation the physical problem of the quantisation of energy appears to be reduced to the purely mathematical one of the determination of the characteristic values of differential equations. This mathematical problem is discussed with examples of the Hermitean polynomial and spherical functions.

CHAPTER VII.—As examples of Schrödinger's mechanics of characteristic values, the linear harmonic oscillator and the rotator with free axis are discussed. In contrast to the older theory, the energy of the oscillator is seen to be an odd multiple of a half energy element, which makes understandable the hypothesis of zero point energy. The angular momentum of the rotator is found to be

$\frac{\hbar}{2\pi}\sqrt{n(n+1)}$. The energy levels in the hydrogen atom

can also be deduced from Schrödinger's equation. The Stark effect is explained in the mathematical theory by the resolution of multiple characteristic values consequent upon the appearance of a disturbing term in a differential equation. For a system consisting of a number of particles, Schrödinger's equation represents a wave in a configuration space, the number of whose dimensions is three times the number of particles.

CHAPTER VIII.—The quantum mechanics founded by Heisenberg, unlike the older quantum theory, is concerned solely with relations between directly observable physical quantities, such as the frequencies and intensities

of spectral lines, and the energy levels of atoms as determined from experiments on electron collision. Heisenberg replaced each periodically variable electron co-ordinate by a square array of partial vibrations with frequencies corresponding with those of the spectral lines and amplitudes given by the intensities of the lines. For such an array of vibrations, Heisenberg gave a definition of multiplication which showed that this operation is non-commutative. The change suffered by the product of a co-ordinate and the corresponding momentum in consequence of an interchange of the factors is equated by Heisenberg's commutation rule to $\hbar/2\pi i$. Application of this relation to the linear harmonic oscillator leads to the result that its energy is an odd multiple of a half energy element, and that Bohr's frequency condition is fulfilled in all quantum jumps.

CHAPTER IX.—Born and Jordan have enabled Heisenberg's programme to be carried out exactly, by the aid of matrix mechanics. By this means, it was shown that the law of conservation of energy and the frequency condition of Bohr follow as necessary results of Heisenberg's commutation rule.

CHAPTER X.—By the application of the conception of the mathematical operator the equivalence of Schrödinger's mechanics of characteristic values and matrix mechanics may be demonstrated. If Heisenberg's commutation rule is transferred to operators, the fundamental equation of Schrödinger is obtained as an extension of classical mechanics.

CHAPTER XI.—While Schrödinger regarded material particles as energy packets, Born on the other hand, from the point of view of quantum mechanics, interpreted the Schrödinger field scalar, propagated in wave form, as the probability of the arrival of a particle at a given place. According to quantum mechanics, causality can

only be accepted for such statistical probabilities, while for the elementary processes of physics it must be denied. This view is supported by Heisenberg's recognition that any measurement of atomic quantities must necessarily be attended by lack of precision.

CHAPTER XII.—Investigation of the angular momentum of a system on the basis of quantum mechanics, in conjunction with the assumption of spinning electrons, leads to the recognition of four quantum numbers expressing the state of an electron. Pauli's principle, according to which two electrons in a single atom can never coincide in all four quantum numbers, gives the maximum number of members of one-, two-, three- and four-quantum electron groups as 2, 8, 18, 32 and so on. An explanation of the periodic system on the basis of the quantum theory is thus given.

CHAPTER XIII.—From the conception of the light quantum gas, as Bose showed, Planck's radiation law may be deduced by regarding the momentum space corresponding to a quantum gas of unit volume as composed of cells of size \hbar^3 , and applying the statistical magnitudes, related in the classical theory to a particle in the n th state, to a cell occupied by n particles. On the basis of Bose's statistics Einstein has constructed a theory of gases differing from the classical theory, which explains degradation at very low temperatures.

CHAPTER XIV.—Pauli's principle was transferred by Fermi to statistics. He founded a new gas theory on the assumption that, in a gas, not more than a single molecule with predetermined quantum numbers could occur. The existence of a zero point energy and a zero point pressure, and also the disappearance of the specific heat at the absolute zero, follow from Fermi's statistics. As Sommerfeld has shown, Fermi's statistics has proved particularly fruitful in its application to the free electrons in metals.

According to Fermi's theory, these represent a completely degraded gas at ordinary temperatures on account of their extremely small mass. In the same way was explained the fact, unintelligible on the basis of classical statistics, that the free electrons make no appreciable contribution to the specific heats of metals.

CHAPTER XV.—A short description is given of further applications of quantum and wave mechanics : the polarisation rule, dispersion, Landé's formula for the resolution of spectral lines in weak magnetic fields, the Paschen-Back effect, the intensity relations of Zeeman components, the helium atom, the Compton effect, the photoelectric effect, homopolar valency, the resonance effect of atomic nuclei in band spectra and the problem of isotopes.

CHAPTER XVI.—The latest development of atomic physics offers the possibility of an essential change in the conceptions of matter, causality and natural law.

LIST OF THE MOST FREQUENTLY OCCURRING SYMBOLS

A	Amplitude.	<i>h</i>	Elementary quantum of action.
D	Diagonal matrix.	<i>i</i>	Index or imaginary quantity.
E	Energy.	<i>k</i>	Boltzmann's constant.
F	Field strength.	<i>j, k, l, m, n</i>	Quantum numbers.
G	Momentum.	<i>m</i>	Mass.
H	Hamiltonian function (or Hermitean polynomial).	<i>p</i>	Component of momentum.
L	Kinetic energy.	<i>q</i>	Co-ordinate.
N	Number of particles.	<i>t</i>	Time.
P	Force.	<i>u</i>	Wave velocity (or specific radiation density).
R	Gas constant.	<i>v</i>	Mechanical velocity.
S	Schrödinger field scalar (or entropy).	<i>w</i>	(In Chapter IV.), a universal velocity.
T	Absolute temperature (or spectral term).	Δ	Laplace derivative.
U	Angular momentum.	β	Abbreviation defined by Equation 8.
V	Potential energy (or volume).	ϵ	Phase constant or individual energy.
W	Probability.	η	Radiation density.
<i>a</i>	Complex amplitude.	λ	Wavelength.
<i>b</i>	Acceleration.	μ	Mass.
<i>c</i>	Velocity of light.	ν	Frequency.
<i>e</i>	Elementary quantum of electricity (or base of natural logarithms).	ϕ	Phase.
<i>g</i>	Group velocity.		

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Elementary quantum of action (<i>h</i>)	$6.545 \cdot 10^{-27}$ erg. sec.
Elementary quantum of electricity (<i>e</i>)	$4.774 \cdot 10^{-10}$ electrostatic units.
Velocity of light (<i>c</i>)	$2.9980 \cdot 10^{10}$ cm./sec.
Mass of the proton	$1.661 \cdot 10^{-24}$ gm.
Mass of the electron	$9.00 \cdot 10^{-28}$ gm.
Boltzmann's constant (<i>k</i>)	$1.372 \cdot 10^{-16}$ erg./degree.

LITERATURE

A complete bibliography would appear to be superfluous, since the more important works have already been referred to in the footnotes. The reader will find a very complete summary of the literature on wave and quantum mechanics at the conclusion of the article by P. Jordan (see p. xvi), "Die Entwicklung der neuen Quantenmechanik," also at the end of the books of Hund and Landé (F. Hund, Linienspektren und periodisches System der Elemente, Berlin, Springer, 1927 ; A. Landé, Die neuere Entwicklung der Quantentheorie, Second Edition, Dresden-Leipzig, Steinkopf, 1926).

The following complete works may be mentioned :

L. DE BROGLIE, *Ondes et Mouvements*, Paris (Gauthier-Villars), 1926.

E. SCHRÖDINGER, *Abhandlungen zur Wellenmechanik* (reprint from *Annalen der Physik*), Leipzig (Barth), 1927.

M. BORN, *Probleme der Atomdynamik*, Berlin (Springer), 1926 ; or *Problems of Atomic Dynamics*, Cambridge U.S.A. (Massachusetts Institute of Technology), 1926.

H. F. BIGGS, *Wave Mechanics, an Introductory Sketch*, London (Humphrey Milford), 1927.

The following papers give summaries of the theory :

L. DE BROGLIE, *Les principes de la nouvelle mecanique ondulatoire*, *Journal de Physique* (6), **7**, 1926, pp. 321-337.

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L. FLAMM, *Die neue Mechanik* (for non-scientific readers), *Naturwiss.* **15**, 1927, pp. 569-578.

K. K. DARROW, *Introduction to Wave Mechanics*, *The Bell System Technical Journal*, **6**, 1927, pp. 653-701 (will also probably appear in the second edition, now in preparation, of K. K. Darrow's *Introduction to Contemporary Physics*, New York, Van Nostrand Co., 1928).

W. HEISENBERG, Quantenmechanik, *Naturwissenschaften* **14**, 1926, pp. 989-994.

A. LANDÉ, Neue Wege der Quantentheorie, *Naturwiss.* **14**, 1926, pp. 453-458.

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L. BRILLOUIN, La nouvelle mecanique atomique, *Journ. de Physique* (6) **7**, 1926, pp. 135-160.

WAVE MECHANICS AND THE NEW QUANTUM THEORY

CHAPTER I

THE PROBLEM OF ATOMIC MECHANICS

THERE is a saying of the great investigator Huygens, belonging to an earlier era of physics, the latter half of the seventeenth century, which not only embodies the scientific tendencies of that time, but also exactly expresses the trend of the next two hundred years. "In true philosophy," says Huygens, "we should conceive the cause of all natural phenomena in terms of mechanics. This we must do, or for ever renounce the hope of understanding anything of physics."*

Actually, the mechanistic tendency in physics remained predominant into the second half of the nineteenth century. It first began to lose its hold when Maxwell, basing his reasoning on the complete failure of all mechanical ether theories, developed his electromagnetic theory of light. The first decades of the twentieth century produced a host of discoveries in the realm of intra-atomic phenomena, and the following up of these phenomena turned the minds of physicists ever more strongly towards the probable relations between mechanical laws and the principles of electricity, magnetism and optics. Reversing Huygens' dictum, the physicist may well say to-day that he must renounce all hope of knowing anything of

* Huygens, *Traité de la Lumière* (Leyden, 1690), Chapter I. : "Dans la vraye philosophie on concoit la cause de tous les effets naturels par des raisons de mechanique. Ce qu'il faut faire a mon avis ou bien renoncer a toute espérance de jamais rien comprendre dans la physique."

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physics until he is able to express mechanical phenomena in terms of the other branches of physics. In pursuance of this object, the theories of de Broglie, Schrödinger and Heisenberg, developed since 1924, have produced advances of the widest significance. These are the theories of which it is hoped to give an elementary account in this work.

Mechanics is the oldest branch of exact physics. It was the branch chosen by the actual founder of theoretical physics, Galileo, for investigation. The statement of its fundamental laws is the work of the man who first attempted to unite the whole of physics into a coherent system on a mathematical basis, namely, Newton. Even after the lapse of two hundred years it seemed as though Newton, in his development of the theories of dynamics, had reached finality, so that, although the formal methods had since been much refined and extended, nothing essentially new could be added to the laws of motion as stated by him. This view was discovered to be premature early in the twentieth century. Between 1905 and 1909 a new mechanics was built up on the basis of the theory of relativity. This brought about, not only a generalisation of the classical laws of motion, which are now seen to be only approximately true in their original form, but also a completely new conception of unusual scope. A remarkable connection was found between mechanics and optics, inasmuch as the velocity of light was seen to be an upper limit to all mechanical velocities, while on the other hand a close connection was discovered between the fundamental mechanical idea of mass and what is probably the most important conception of general physics, that of energy. On the basis of the new mechanics of relativity, these two fundamental conceptions were shown to be identical, since the mass of a body or a material particle differs from its energy content only by a universal proportionality factor which is equal to the square of the velocity of light.

It was not, however, only the theory of relativity which

shook the foundations of classical mechanics. They were also found to be at variance with some of the essential results of the quantum theory, which was developed at about the same time as the theory of relativity. Like that theory, the quantum theory is not merely an isolated field, but it forms the foundation of all physics. It had its beginning in the discovery of a far-reaching parallelism between mechanical, electrical and optical phenomena. Even in the last years of the nineteenth century it had become clear that the bodies involved in all dynamical processes must ultimately be composed of two kinds of fundamental particles, whose masses were two universal constants, and that all atoms must be formed of these two kinds of original particles, now distinguished as protons (with the larger mass) and electrons (with the smaller mass). Towards the end of the nineteenth century also, the atomic structure of electricity became recognised. Physicists learnt that all electrical charges must be multiples of an elementary charge, and that all the ultimate particles of matter must possess such an elementary charge, the heavier protons being positively, the lighter electrons negatively charged.*

To the discovery of the ultimate particles and the elementary electrical charge was added at the beginning of the twentieth century the no less important discovery that light (in the widest sense of the word) also possesses an atomic structure, so that it is possible to some extent to talk of "light atoms." By light must be understood, not only visible light rays, but also the infra-red heat rays, the waves produced by electrical discharges, "wireless" waves, ultra-violet rays, Röntgen rays, the γ -rays of radio-active substances, and so on. All these rays, apparently so diverse in character, are now known to be similar in their nature, and to differ only in their

* The mass of a proton is $1 \cdot 66 \cdot 10^{-24}$ gm. : the mass of an electron is 1,847 times smaller, $9 \cdot 00 \cdot 10^{-28}$ gm. The elementary charge of electricity is $4 \cdot 77 \cdot 10^{-10}$ electrostatic units (by an electrostatic unit is meant that charge which exerts a force of 1 dyne upon a similar charge at a distance of 1 cm.).

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vibration frequency, which is, for example, of the order of 4×10^{14} per second for red light, 1×10^{18} for the hardest X-rays, and only a few hundred thousands for the ordinary electric waves employed in radiotelephony.

It was discovered by Planck in 1900, and more fully worked out in 1905 by Einstein, that light and all similar radiation is composed of radiation elements whose energy is connected with the frequency of the radiation by a universal proportionality factor. Quite generally, the energy of an element of radiation may be obtained, in ergs,* by simply multiplying the vibration frequency per second by the number $6.55 \cdot 10^{-27}$. This number has the physical dimensions of energy divided by frequency, *i.e.*, of energy multiplied by time. Such a product is known in mechanics as "action," and the universal factor expressing the proportionality between energy and frequency is therefore called the elementary quantum of action. The energy of an element of yellow light thus work out at $3.3 \cdot 10^{-12}$ ergs.

It has been definitely shown by numerous experiments that the elements of radiation, to-day known as light quanta, or more recently also as photons, have an individual existence just as real as that of the protons or electrons. In the so-called photoelectric effect, when clouds of electrons are liberated from a metal plate by illumination with ultra-violet light or X-rays, it is found that the energy of each photon is converted into the kinetic energy of a corresponding liberated electron. Conversely, during the production of X-rays by cathode rays (rapidly moving electrons) each individual photon arises from the disappearing kinetic energy of a corresponding electron.

On account of the identity of energy and mass already mentioned, each photon has a definite mass, which is also directly proportional to its frequency.† This mass may

* The work performed in raising a weight of 1 kg. through 1 metre is equal to $9.81 \cdot 10^7$ ergs.

† It must, however, be remembered that in the sense of the theory of relativity the mass of the photons would vanish at zero velocity : see later, equation (43).

be obtained in grams by multiplying the frequency (per second) by the number $7 \cdot 27 \cdot 10^{-48}$ (this number is equal to the elementary quantum of action divided by the square of the velocity of light). For visible light, the mass of a photon is very small compared with the mass of an electron, being some hundred thousand times smaller. For the photons of γ -rays, however, the mass is approximately equal to that of an electron. The fact that the photons do indeed actually possess an individual mass may most clearly be seen from the results of collisions between light quanta and electrons. As Arthur H. Compton discovered in 1923, not only is the law of the conservation of energy obeyed in such collisions, but also the law of the conservation of momentum ; the latter is given, in the case of the electron and also in that of the photon moving with the velocity of light, by the product of the mass and the velocity.

Although the elementary quantum of action was actually introduced into physics as an optical constant (namely, as that universal constant which governs the atomic nature of light), physicists soon discovered that purely mechanical processes occurring within the atom must also be determined by the elementary quantum of action. What was originally a purely optical constant thus also took on the second function of a fundamental constant of atomic mechanics.* The necessity of an atomic mechanics was also shown by the discovery that all atoms contain a positively charged nucleus surrounded by negative electrons.† Between the nucleus and its surrounding electrons there must therefore be an electrical attraction ; the permanent existence of such an atom

* The author believes himself to have been the first to develop this idea, in the year 1910, with reference to the hydrogen atom (*Sitz.-Ber. d. Wiener Akad. d. Wiss., math. nat. Kl.*, IIa, 1910, pp. 119-144). In this publication the connection between the fundamental constant of spectroscopy (the so-called Rydberg constant) and the elementary electrical charge, the mass of the electron and the elementary quantum of action, was first deduced.

† The conception of a "nuclear atom" propounded by Rutherford in 1911, finds its strongest experimental support in observations on the penetration of metal foil by α -rays.

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therefore seemed capable of explanation only by the assumption of centrifugal forces. It was therefore assumed that the electrons are in rapid motion round the nucleus, like the planets in the solar system, with which the atoms were readily compared.

The simplest problem of atomic mechanics was presented by the hydrogen atom, in which, on the basis of many experimental facts, only a single planetary electron was assumed. The radius of the electron path in such an atomic model at first appeared to be indeterminate. Bohr overcame this difficulty in 1913 by means of a hypothesis which proved to be extraordinarily fruitful for the further development of atomic physics. This hypothesis consisted in setting 2π times the angular momentum of the electron in its orbit (determined by the product of the mass of the electron, the radius of the orbit and the velocity) equal to the elementary quantum of action. In conjunction with the fact that the centrifugal force and electrical attraction must balance each other, Bohr's hypothesis gave quite definite values for the orbital radius and velocity in the model employed.*

On the other hand, however, spectroscopical observations show that each atom of a chemical element possesses a multitude of quite definite values of light frequency, which, taken together, determine the so-called line spectrum of the element in question. The lines may occur both as lines of emission and also of absorption, *i.e.*, the atom can both give out and absorb photons of definite frequency. According to the principle of conservation of energy, the first process must obviously be associated with a loss, the second with a gain of energy within the atom. From the proportionality between the energy of a photon and its frequency, it follows that such an atom can change its energy only by quite definite amounts, characteristic of the chemical element in question.

* On the basis of Bohr's hypothesis, a value of $5 \cdot 30 \cdot 10^{-9}$ cm. is obtained for the orbital radius, and a value of $2 \cdot 188 \cdot 10^8$ cm. per sec. for the velocity. The number of revolutions per second amounts to $6 \cdot 58 \cdot 10^{15}$.

Actually, it is also shown by observations of collisions between electrons and atoms * that the electrons can only give up to the atoms quite definite and measurable amounts of energy. A further result of these experiments is that in certain circumstances the transference of energy to the atom may give rise to the emission of a spectral line whose frequency is exactly equal to the amount of energy given up, divided by the elementary quantum of action. The important fact thus emerges, that atoms may exist both in their normal state and also in other states containing additional quite definite increments of energy. Transitions between these energy stages which are characteristic of each element are the cause of the emission or absorption of definite spectral lines.

Bohr arrived at a satisfactory explanation of the observed spectrum of hydrogen by the assumption that, in the abnormal states of the hydrogen atom 2π times the angular momentum is equal, not to the elementary quantum of action itself, but to an integral multiple of it. The series of atomic states is thus obtained, according to Bohr, by equating the quotient of 2π times the angular momentum and the elementary quantum of action to the series of whole numbers 1, 2, 3, etc. Thus, Bohr's method essentially consisted in first determining all the possible orbits in the atom on the basis of classical mechanics, and then choosing from the total number, as fulfilling the quantum condition, those orbits which satisfied the relation given above.

This method of Bohr was subsequently completed and further developed, particularly by Sommerfeld, and has proved extraordinarily fruitful for the further advancement of theoretical physics. It made possible within a decade the elaboration of a general theory which was able to explain almost all known spectroscopical facts in a consistent manner. As the problems of atomic physics increased in number, physicists eventually found cases

* Experiments on electronic collisions were first undertaken by Franck and Hertz in 1913.

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where the method of Bohr failed. Thus, for example, it was found impossible by means of the method to explain the helium atom in accordance with experiment, although this atom is, next to the hydrogen atom, the simplest.

The occasional failure of the Bohr theory turned the attention of physicists once more to the fundamental difficulties which had been attached to it from the beginning, but which had been forgotten in the years of its triumphant application. Now, repeated failure of the theory brought these difficulties again to the fore. The choosing of the "quantised" orbits was still quite incomprehensible from the standpoint of classical mechanics, as was to no less a degree the determination of the mechanical orbits by a fundamental optical constant. The only hope of extricating the atomic theory from the *impasse* in which it found itself in 1923 lay in the discovery of a fresh generalisation, a third foundation of mechanics, if it may be so called, which in its new form should include as special cases, not only the first mechanics of Galileo, but also the second mechanics of Einstein.

The mechanics of Einstein gave rise to further knowledge in the case of very high velocities, while classical mechanics remained true for ordinary velocities. Similarly, it must be demanded of the third mechanics that it should lead to new results when applied to the region of atomic dimensions, while in its application to ordinary macroscopic dimensions its results should coincide with those of classical mechanics. On these lines it might be hoped that the new mechanics might yield of itself the hitherto mysterious quantum conditions governing atomic phenomena, so that these need no longer be regarded as foreign additions without any immediate connection with the other facts. In this way the new mechanics might also put an end to the difficulties which had arisen from the earlier quantum theory owing to the fact that many of its results stood contradicted by experimental observations.

CHAPTER III

FERMAT'S PRINCIPLE, THE LORENTZ TRANSFORMATION AND THE CONCEPTION OF GROUP VELOCITY

BOTH in mechanics and in optics the attempt has been made from early times to discover a general guiding principle which should epitomise the fundamental laws of those sciences in the simple form of a maximum or minimum condition for the magnitudes concerned. In optics such a principle was established in the seventeenth century by Fermat. This principle teaches that a ray of light, in passing from a point A to a point B, takes that path which will make the time of transit a minimum.*

From Fermat's principle it is easy to deduce, for example, the law of refraction, according to which the sine of the angle of incidence bears to the

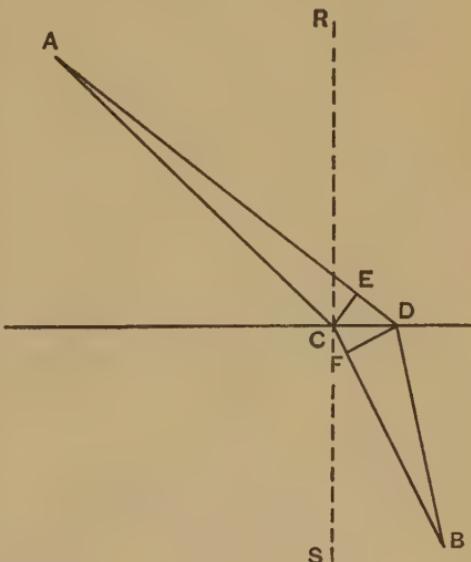


FIG. 1.

* Fermat's principle is associated with an older law, which was already known in antiquity to Hero of Alexandria for the special case of the reflection of light, in which the length of the path is given as a minimum. Since for reflection the velocity has the same value at all points of the path, the shortest time in this case corresponds to the shortest path.

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sine of the angle of refraction the same ratio as the velocity of the waves in the first medium to the velocity in the second medium. Let C and D (Fig. 1) be two adjacent points in the surface separating two media, and let E and F be the feet of the perpendiculars dropped from the two points C and D on to the rays AD and CB. Let the intervals required by light to pass along the paths ACB and ADB be t_1 and t_2 , and let the velocities of light in the two media be u_1 and u_2 . Then it follows from Fig. 1 that

$$t_2 - t_1 = \frac{DE}{u_1} - \frac{CF}{u_2}.$$

If we denote the angle of incidence (ACR) by α and the angle of refraction (BCS) by β , and remember that C and D are adjacent points, we may also write

$$t_2 - t_1 = CD \left(\frac{\sin \alpha}{u_1} - \frac{\sin \beta}{u_2} \right).$$

If now the actual path followed by the ray passes through C, the value of t_1 must be the minimum value already mentioned. In mathematical language this means that the difference $(t_2 - t_1)$ must be vanishingly small in the second order when the length CD becomes vanishingly small in the first order. This is only possible when the expression in brackets, by which the length CD is multiplied in the last equation, is equal to zero, *i.e.*,

$$\frac{\sin \alpha}{\sin \beta} = \frac{u_1}{u_2},$$

which is identical with the ordinary law of refraction.

Thus, if we consider two media in which the velocities are u_1 and u_2 , and denote by s_1 and s_2 the lengths of the paths traversed by the ray in passing from A to B through the two media, the time $(s_1/u_1 + s_2/u_2)$ occupied in its passage will be a minimum. For a non-homogeneous medium, in which, in general, the velocity varies from place to place, it is necessary to find an expression for the

time of travel of the ray by splitting the path into elements, dividing each of these elements by the corresponding velocity, and summing all the quotients so obtained. We thus obtain, in mathematical language, the line-integral between A and B' of the reciprocal of the velocity. Using the ordinary mathematical notation we then have the relation.

$$\int_A^B \frac{ds}{u} = \text{a minimum} \quad \dots \quad \dots \quad (1)$$

(where u = velocity of the waves).

This relation, the general expression of Fermat's principle, is remarkably closely connected with a formula developed in the middle of the eighteenth century as a guiding principle of mechanics. This formula is due to Maupertuis, although it was actually put into more exact form by Euler somewhat later. According to this principle, the actual motion of a particle from A to B is governed by the condition that the line-integral of the mechanical velocity (v) over the path in question, is a minimum.* That is to say, the following relation holds

$$\int_A^B v \, ds = \text{a minimum}, \quad \dots \quad \dots \quad (2)$$

where v is the mechanical velocity. From this formula it is actually possible to derive the fundamental equations of mechanics, and the determination of the path is also directly possible. The parabolic path of the flight of a projectile may, for example, be obtained by its use.

In Maupertuis' theorem the mechanical velocity thus plays the same part as the reciprocal of the wave velocity in Fermat's principle. Now Fermat's principle is, subject to certain conditions, a general principle approximately true of all kinds of waves. A comparison of equations (1) and (2) thus offers the possibility of explaining mechani-

* In special cases the integral may be a maximum; the theory only requires that it shall be an "extreme" value.

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cal regularities on the principles of the theory of waves. It is evident, in fact, that the fundamental principles of mechanics follow directly from Fermat's principle if it is assumed that the phenomena of motion depend upon some undulatory process in which there is a universal proportionality between the mechanical velocity and the reciprocal of the wave velocity. In order that this connection may be discussed, a short and quite elementary treatment of the general wave formula will first be interpolated.

Any undulatory process may be described by considering any given point in the path of the wave as executing a vibration. Such a process may be written in its simplest form

$$S = A \sin (2\pi\nu t) \quad (3)$$

where S represents the varying quantity,* A the amplitude, ν the frequency and t the time. The quantity S given by equation (3) always returns to the same value,† when the time has increased by $1/\nu$. If, therefore, we write equation (3) in the form

$$S = A \sin \phi, \quad (4)$$

ϕ may be called the *phase* of the vibration. The simple form of equation (3) can, however, only be used when the time is measured from the instant at which S is zero. This condition is, in general, impossible when several simultaneously occurring vibrations are under consideration ; in this case a further constant must be added to the term representing the phase.

* The varying quantity may be a distance or an angle (as, for example, in the vibration of a pendulum), but it may also be a density, or an electric or magnetic field strength, or a temperature, etc. A vibratory motion about a point of rest (after the manner of a pendulum), is the clearest example of a vibratory process ; it is, however, quite unnecessary and unjustifiable on this account to picture any vibratory process consisting in the periodic variation of a physical quantity as a mechanical oscillation.

† For $\sin \left[2\pi\nu \left(t + \frac{1}{\nu} \right) \right] = \sin (2\pi\nu t + 2\pi) = \sin (2\pi\nu t)$.

The time periodicity characteristic of a vibratory process is supplemented in the case of a wave motion by a periodicity in space. The propagation of a wave in a given direction (which may be taken as the x -axis) is characterised by the fact that at a distance x_1 from any arbitrarily chosen origin ($x = 0$) the conditions are always exactly the same as those occurring at the origin t_1 seconds later, when the product of t_1 and the wave velocity u is equal to the distance x_1 . Thus $t_1 = x_1/u$, and we obtain the condition of vibration at any given spot x at the time t by replacing the quantity t in equation (3) by the expression $(t - x/u)$. We thus obtain the wave formula

$$S = A \sin \left[2\pi\nu \left(t - \frac{x}{u} \right) \right] \dots \dots \quad (5)$$

The phase is thus determined by the expression in square brackets, to which in general a further phase constant ϵ must be added. In addition the distance x from the origin must usually be replaced by the length s of the ray measured from a fixed point. The expression for the phase then becomes

$$\phi = 2\pi\nu \left(t - \frac{s}{u} \right) + \epsilon \dots \dots \quad (6)$$

Now there is a remarkable, and, until fairly recently, hardly noticed connection between the wave formula and one of the fundamental formulæ of the theory of relativity, the Lorentz Transformation. As is well known, Einstein's theory of relativity depends on the assumption that all time data are only relative ; that they depend on the position of the observer who is describing them, and that therefore they differ for two observers who are moving with respect to one another. The theory of relativity furthermore postulates such a connection between the position and the time data of the two observers that for both of them light travels away

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from them equally in all directions and with the same velocity.*

For the special case of uniform rectilinear motion this connection may be expressed in the form of the so-called Lorentz Transformation. If the two observers are moving relatively to one another with a velocity v in a direction which we may take as that of the two x -axes, then the spatial co-ordinates and time data used by the two observers are connected by the equations †

$$x' = \beta(x - vt); \quad y' = y; \quad z' = z; \quad t' = \beta \left(t - \frac{v}{c^2}x \right) \quad . \quad (7)$$

where c is the velocity of light, and β is given by the expression

$$\beta = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The connection between the two relative times in equation (7) is of special interest with regard to the wave formula. Thus, if we replace the mechanical velocity v by another velocity u , related to it by the equation

$$uv = c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

we may write the fourth of equations (7) in the form

$$t' = \beta \left(t - \frac{x}{u} \right); \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

the close resemblance of this to the wave formula may be seen at once.

In order to realise the significance of the last equation, let us now consider any vibratory process, associated in some way with a moving body. Let the velocity, referred

* This follows from the experimental fact that the motion of the earth has no influence on the propagation of light over the earth's surface.

† By introduction of the values from equation (7) the expression $(x'^2 + y'^2 + z'^2 - c^2t'^2)$ becomes identical with $(x^2 + y^2 + z^2 - c^2t^2)$, while the equation

$$x^2 + y^2 + z^2 - c^2t^2 = 0$$

expresses the fact that light is propagated uniformly in all directions with the velocity c .

to a given system of co-ordinates, be v . This system of co-ordinates we regard as "fixed" (x, y, z, t) , while we regard as "moving" another system (x', y', z', t') in relation to which the body is at rest. The moving coordinate system thus moves in relation to the first system with the velocity v , in the direction of the common x -axis. With regard to this system of moving co-ordinates, the vibratory process is represented by the equation

$$S = A \sin (2\pi\nu't').$$

By making use of equation (10), and for the sake of simplicity putting

$$\beta\nu' = \nu \dots \dots \dots \quad (11)$$

we obtain as a result of the Lorentz Transformation

$$S = A \sin \left[2\pi\nu \left(t - \frac{x}{u} \right) \right].$$

On the basis of this equation any vibratory process connected with a moving body may therefore be regarded as a wave motion whose velocity of propagation is equal to c^2/v , where c is the velocity of light and v is the mechanical velocity.

Now, according to one of the fundamental relations of the theory of relativity, a mechanical velocity can never be greater than the velocity of light, or indeed equal to it. The propagation of a wave such as we have been considering must, therefore, always take place with a velocity greater than that of light. Such an idea seems at first to involve a great difficulty, since the velocities of moving bodies are quite different from the velocities of propagation of the waves which one has to regard as associated with the bodies. For a fast motor car, whose speed perhaps amounts to one ten-millionth of the velocity of light, the waves are some 10^{14} times faster than the car itself; for a pedestrian the discrepancy is still greater. The apparent contradiction can, however, be satisfactorily overcome by means of a consideration already known for many years to theoretical physicists, both in

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optics and in hydrodynamics, which has led to the important conception of “*group velocity*.”

A system of waves whose frequencies differ from one another within definite limits is known as a “*wave group*.” The nature of such a wave group may be understood by keeping in mind the fact that the mean value of the sines of all possible angles, taking the signs into account, is zero, since to each positive value of the sine there corresponds an equal negative value which cancels it. If, therefore, we consider a group of vibrations whose phases do not correspond, the resulting vibration, obtained by summing the products of the amplitudes and the sines of the corresponding phase angles, is in general very small compared with the algebraic sum of the amplitudes themselves.

Let us now consider a part of a wave group where there is a fairly complete agreement of phase among the single waves belonging to the group ; the resultant vibration is in consequence relatively large. Such a place, where the energy density is a maximum compared with the surroundings, we will call a “*centre of energy*” of the wave group. It is evidently characterised by the fact that, for two waves differing in frequency by an infinitesimal amount, the phase difference is vanishingly small in the second order, *i.e.*, at a centre of energy the partial differential coefficient of the phase with respect to the frequency must vanish, or

$$\frac{\partial \phi}{\partial \nu} = 0. \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (12)$$

By writing for ϕ the value in equation (6), and applying the ordinary rules of differentiation, we obtain

$$\frac{\partial \phi}{\partial \nu} = 2\pi t - 2\pi s \frac{d\left(\frac{\nu}{u}\right)}{d\nu} + \frac{d\epsilon}{d\nu}.$$

From this, and equation (12)

$$s = \frac{1}{d\left(\frac{\nu}{u}\right)} \left(t + \frac{1}{2\pi} \frac{d\epsilon}{d\nu} \right).$$

The quantity s is thus dependent on time, *i.e.*, the centre of energy itself moves with a velocity equal to the factor multiplying the expression in brackets in the last equation. For, if we call this factor g , the differential co-efficient of the distance with respect to time, in other words the velocity, as given by the last equation, is seen to be also g . The quantity g thus represents the velocity with which the centres of energy move, and thus also the velocity with which the energy of the waves is propagated. It is therefore called the “*group velocity*” of the waves, and must be distinguished from the wave velocity in cases where the latter depends on the frequency (*i.e.*, where there is dispersion). From the last equation the following relation for the group velocity may be obtained *

$$\frac{1}{g} = \frac{d\left(\frac{\nu}{u}\right)}{d\nu} \dots \dots \dots \quad (13)$$

We will now consider this equation with special reference to the waves, already mentioned, which move with a velocity greater than that of light. The law of dispersion for these waves is contained in equations (11) and (8). If we write ν_0 for the frequency (which is independent of the velocity) represented in equation (11) by ν' †, we obtain

$$\nu = \frac{\nu_0}{\sqrt{1 - \frac{v^2}{c^2}}} \dots \dots \dots \quad (14)$$

* If we carry out the differentiation in equation (13) we obtain

$$\frac{1}{g} = \frac{1}{u} - \frac{\nu}{u^2} \frac{du}{d\nu}$$

From this we see that in the absence of dispersion, but only then, the group velocity and the wave velocity are equal.

† ν_0 is the frequency referred to a system of co-ordinates which moves with the body.

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According to equation (9), for the super light waves

$$\frac{v}{u} = \frac{vv}{c^2},$$

and therefore

$$\frac{d\left(\frac{v}{u}\right)}{dv} = \frac{v}{c^2} + \frac{v}{c^2} \frac{dv}{dv}.$$

But from equation (14)

$$\frac{dv}{dv} = \frac{v_0 v}{c^2 \left(1 - \frac{v^2}{c^2}\right)^{\frac{3}{2}}} = \frac{vv}{c^2 - v^2}.$$

Therefore

$$\frac{d\left(\frac{v}{u}\right)}{dv} = \frac{v}{c^2} + \frac{c^2 - v^2}{c^2 v} - \frac{1}{v}.$$

From this, together with equation (13), follows the important result that

$$g = v \dots \dots \dots \quad (15)$$

If, therefore, we consider a vibratory process associated with a moving body, this vibration may be regarded, on the basis of the Lorentz Transformation, as a super light wave whose group velocity is equal to the mechanical velocity of the material particle.

CHAPTER III

THE WAVE MECHANICS OF DE BROGLIE

THE relations discussed in the previous chapter are deduced throughout from the older principles of mechanics and optics, from general considerations of the theory of waves, and from the theory of relativity. A great service was rendered by Louis de Broglie when, in 1924, he realised the full significance of these previously neglected relations ; he thereby became the founder of a new theory which has had the greatest influence upon the subsequent development of physics. De Broglie made the fundamental assumption that with every material particle there is associated a vibratory process characterised by the fact that the elementary energy of the vibration (*i.e.*, the product of the frequency and the elementary quantum of action) is equal to the intrinsic energy of the particle, or, according to the relativity theory, equal to the product of the mass and the square of the velocity of light.

From what has been said in the previous chapter, it thus appears that every moving particle of matter is associated with a wave which is propagated with a velocity greater than that of light, but whose group velocity represents the mechanical velocity of the particle. The regularities governing this motion, which are expressed in Maupertuis' principle, need thus no longer be regarded as isolated axioms, but follow from de Broglie's theory as the necessary consequence of a general wave principle. Matter itself appears to be resolved into waves whose centres of energy are the electrons and protons ; the theory founded by de Broglie may be described as *wave mechanics*, and the super light waves as *material waves*.

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From what has been said already, the fundamental equation of wave mechanics is seen to be

$$h\nu = mc^2. \dots \dots \dots \quad (16)$$

where m is the mass of the material particle and h the elementary quantum of action. If we write for m the mass of an electron, the associated frequency is seen to be $1.24 \cdot 10^{20}$ (per second). In the case of the proton, with 1,847 times the mass, it is $2.29 \cdot 10^{23}$. Since the frequency and the mass are proportional, the frequency, dependent on the velocity like the mass, varies only within narrow limits, except in the case of motion whose velocity is of the order of that of light. In the case of material waves, as with any other kind of wave, the wavelength and frequency are connected by the condition that their product is equal to the velocity of propagation, *i.e.*, that

$$u = \lambda\nu \dots \dots \dots \quad (17)$$

or, according to equation (9)

$$\lambda = \frac{c^2}{\nu\nu}.$$

It thus follows from equation (16) that

$$\lambda = \frac{h}{mv}. \dots \dots \dots \quad (18)$$

The wavelength in the case of an electron may thus be found by dividing the number 7.28 by the velocity of the electron (in centimetres per second). For velocities ranging from 20 to 40 per cent. of the velocity of light (cathode rays, for example) λ is of the order of 10^{-9} cm. For the relatively slower electrons emitted by incandescent wires, λ is of the order of 10^{-7} cm., *i.e.*, of the same order of magnitude as the waves of soft Röntgen rays. Since the product of the mass and the mechanical velocity represents the momentum G , equation (18) may be written in the form

$$G = \frac{h}{\lambda} \dots \dots \dots \quad (19)$$

or, using equation (17)

$$G = \frac{h\nu}{u} \quad \dots \quad \dots \quad \dots \quad (20)$$

Let us next consider a periodic motion in a closed orbit. Let dr be an element of the orbit which we may identify with an element ds of the ray. Then, at a given instant the local difference of phase at the two extremities of an element of the orbit is, according to equation (6)

$$d\phi = -2\pi\nu \frac{dr}{u}.$$

If A and B are two points in the closed orbit, and if, at a given instant, ϕ_1 is the phase at A, then we obtain for the phase at B the expression

$$\phi_2 = \phi_1 - 2\pi \int_A^B \frac{\nu dr}{u}.$$

If we now steadily increase the portion of the orbit comprised between the points A and B, the point B must eventually coincide once more with A, since the orbit is a closed one. At the point A, however, the pulsating magnitude can only have a single determinate value, and consequently when B coincides with A,

$$\sin \phi_2 = \sin \phi_1.$$

This is, in general, only possible when

$$\phi_2 - \phi_1 = \pm 2n\pi,$$

where n is an integer. If we designate the integral taken over the whole closed orbit by the usual symbol \oint , it is seen that

$$\oint \frac{\nu dr}{u} = n \quad \dots \quad \dots \quad \dots \quad (21)$$

or (from equation 20)

$$\oint G dr = nh \quad \dots \quad \dots \quad \dots \quad (22)$$

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The last two equations assume a particularly simple form for the special case of a constant velocity, such as that, for example, of uniform motion in a circle. Here the wave velocity is constant, as is also the frequency, on account of the constancy of the mass. By applying equation (17), equation (21) may be written in the form

$$\oint dr = n\lambda; \quad \dots \dots \quad (23)$$

in other words, for a constant velocity, only those closed orbits are possible for which the length of the orbit is an integral multiple of the wavelength. This regularity may also be expressed in another way by the use of equation (22). For constant mass and velocity, this equation assumes the form

$$2a\pi G = nh,$$

where a is the radius of the orbit. For the angular momentum, U (the product of the momentum and the radius of the orbit), the following relation therefore holds

$$2\pi U = nh. \quad \dots \dots \quad (24)$$

The only possible orbits are therefore those for which 2π times the angular momentum is an integral multiple of the elementary quantum of action. This statement, which is merely another expression of equation (23), is thus identical with the previously mentioned fundamental quantum rule with which, in 1913, Bohr succeeded in interpreting the hydrogen spectrum. It actually follows as a strict necessity from the assumption of material waves, and the same is true also of the general equation (22), from which the ordinary quantum rules for the more general problem may be derived.*

As Einstein realised, another necessary consequence of de Broglie's theory is a quantisation of the translational energy of a gas enclosed in a vessel. This result, which is of the greatest significance in thermodynamics and the

* See Einstein, *Verh. d. Deutsch. Physik. Ges.*, 19, 1917, p. 82.

kinetic theory of gases, may be derived by a general method which was used by Lord Rayleigh as early as 1900, and developed more accurately by Jeans in 1905. The method depends on the conception of "characteristic vibrations." For the sake of simplicity, the closed space under consideration may be regarded as a cube. The starting-point is the fact that, along a stretched wire of

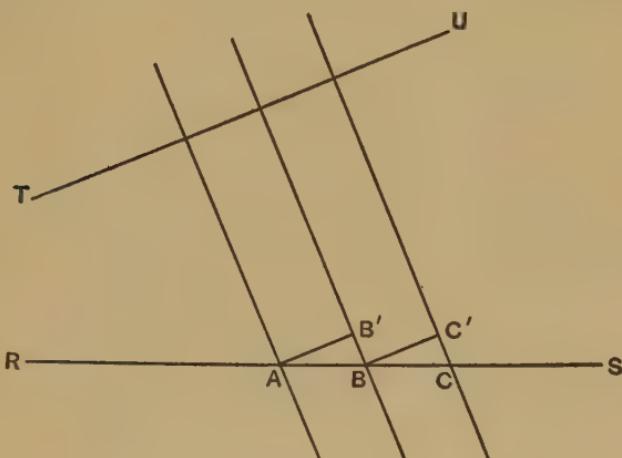


FIG. 2.

length l , stationary vibrations are only possible for those wavelengths which satisfy the equation

$$l = n \frac{\lambda}{2}$$

for integral values of n , the so-called subdivision number. In a cube, instead of the nodal points there are nodal planes parallel to the sides of the cube.

Let us now imagine a system of co-ordinates whose origin coincides with one of the corners of the cube, and whose axes are three of the sides of the cube. Let the subdivision numbers along the x -, y - and z -axes be n_1 , n_2 , and n_3 , and let RS be any straight line parallel to the x -axis, cut by successive nodal planes running parallel to the y - and z -axes in the points A, B, C. The distances be-

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tween the nodal planes are a/n_1 , where a is the length of the side of the cube. Now let TU be any ray which makes angles α, β, γ with the three axes. Through the points A, B, C draw the plane wave-fronts ; these must be normal to the ray, and must differ in phase by half a period, since this is the difference existing at the points A, B, C which belong to the three wave-fronts. Thus,

$$AB' = BC' = \frac{\lambda}{2}.$$

But further,

$$AB' = AB \cos \alpha = \frac{a}{n_1} \cos \alpha.$$

Since analogous relations must also hold for the y - and z -axes, we obtain the three equations

$$\left. \begin{aligned} \frac{2a}{\lambda} \cos \alpha &= n_1 \\ \frac{2a}{\lambda} \cos \beta &= n_2 \\ \frac{2a}{\lambda} \cos \gamma &= n_3 \end{aligned} \right\} \quad \dots \quad (25)$$

By squaring these equations and adding, we obtain

$$\frac{2a}{\lambda} = \sqrt{n_1^2 + n_2^2 + n_3^2} \quad \dots \quad (26)$$

(since the sum of the squares of the three cosines equals 1). Equations (25) can therefore be written in the form

$$\left. \begin{aligned} \cos \alpha &= \pm \frac{n_1}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \\ \cos \beta &= \pm \frac{n_2}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \\ \cos \gamma &= \pm \frac{n_3}{\sqrt{n_1^2 + n_2^2 + n_3^2}} \end{aligned} \right\} \quad \dots \quad (27)$$

(In Fig. 2 the ray TU might also be in the opposite symmetrically disposed position with regard to RS). We thus

see from equations (26) and (27) that each of the triplet groups of numbers n_1, n_2, n_3 corresponds to a characteristic vibration of definite wavelength and definite orientation. Conversely, only those vibrations are possible for which the values of $\lambda, a, \beta, \gamma$ satisfy equations (26) and (27) for integral values of n_1, n_2, n_3 .

Knowing this, we may readily deduce an important result with the aid of a simple geometrical construction. Let us consider a system of rectangular co-ordinates which contains only the positive halves of the axes, and thus encloses only one-eighth of the whole space. Imagine in this space a point lattice whose lattice constant is of unit length, as shown in plan in Fig. 3. All the points have then integral co-ordinates, and conversely any characteristic vibration given, in equations (26) and (27), by a certain triplet of whole numbers may be represented by that point of the lattice whose co-ordinates are equal to the three numbers. The distance of this point of the lattice from the origin is

$$r = \sqrt{n_1^2 + n_2^2 + n_3^2},$$

and therefore, from equation (26)

$$r = \frac{2a}{\lambda}$$

or

$$r = 2az \quad \dots \quad \dots \quad \dots \quad \dots \quad (28)$$

where z is the so-called *wave number*, which represents the number of wavelengths in unit length.

The construction of our lattice now gives an immediate answer to the question, how many characteristic vibrations are possible within the range of wave numbers from z to $z + \Delta z$. This number, which we may write ΔZ , is equal to the number of lattice points in the space between two

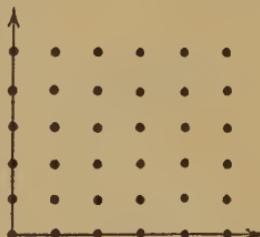


FIG. 3.

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spherical surfaces of radii $2az$ and $2a(z + \Delta z)$. Now, on an average there is one lattice point in each unit volume, since the lattice constant has been taken as unit length, and therefore ΔZ is simply equal to one-eighth of the volume of the spherical shell enclosed by the two spherical surfaces, *i.e.*, to

$$\frac{1}{8}4r_1^2\pi(r_2 - r_1),$$

where

$$r_1 = 2az, r_2 = 2a(z + \Delta z).$$

We thus find that

$$\Delta Z = 4\pi V z^2 \Delta z \quad \dots \quad (29)$$

where V is the volume of the cube under consideration. This formula, here deduced only for the simple case of a cube, but actually quite independent of the nature of the space, was first worked out, as has been said, by Lord Rayleigh, and later and more accurately by Jeans.

We will now apply the Rayleigh-Jeans formula, which is true both for electromagnetic and for elastic waves (*i.e.*, both for light and sound waves), to the material waves of the gas in an enclosed space. According to equation (19), the wave number in this case is equal to the quotient of the momentum of a material particle and the elementary quantum of action, and therefore ΔZ represents the number of possible values of the momentum G in the interval from G to $G + \Delta G$. We therefore replace z by G/h , and obtain

$$\Delta Z = \frac{4\pi V}{h^3} G^2 \Delta G \quad \dots \quad (30)$$

Since G is the product of the molecular velocity v and the molecular mass m , we may further regard ΔZ as the number of possible values of the velocity which lie in the interval from v to $v + \Delta v$, and we then find

$$\Delta Z = \frac{4\pi V m^3}{h^3} v^2 \Delta v \quad \dots \quad (31)$$

Let us consider, for the sake of example, helium at room

temperature. We then have to make the value of m/h about 1,000, and v about 10^5 . For a volume of 1 c.c. and a velocity range of 1 cm./sec. equation (31) then gives a number of the order of 10^{20} , though for a cube of side 10^{-6} cm. the corresponding number is only of the order of one hundred. Thus, on the basis of de Broglie's theory, the translational movements of the molecules of a gas in a closed space are also seen to obey quantum relations, just like periodic movements in closed orbits. As a matter of fact, the idea of a quantisation of translational energy was developed as early as 1916 by Planck,* who employed it successfully for various thermodynamical calculations (e.g., the calculation of the so-called chemical constants of gases). This hypothesis, which was hitherto entirely unintelligible, thus appears as a necessary result of the theory of material waves.

A readily intelligible explanation of equation (31) may be given by representing the momenta of the molecules in a three-dimensional momentum space, in which each molecule is represented by a representative point whose co-ordinates are the components of the momentum of the molecule (mv_x, mv_y, mv_z). The distance of the representative point from the origin then gives the value of the momentum (*i.e.*, the quantity mv). Thus, if in the momentum space we draw two concentric spherical surfaces with centre at the origin and radii mv and $m(v + \Delta v)$, the spherical shell enclosed by the two surfaces, of volume $4\pi m^3 v^2 \Delta v$, contains all the representative points whose values lie between mv and $m(v + \Delta v)$. According to equation (31), the number of representative points in unit volume of this space is

$$s = \frac{V}{h^3}$$

Conversely, we may regard the momentum space as divided up into cells of size

$$\sigma = \frac{h^3}{V} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \quad (32)$$

* *Sitz.-Ber. d. Akad. d. Wiss.*, Berlin, 1916, p. 653.

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so that within each cell no difference of momentum value can be distinguished ; within each cell, therefore, only a single value of the momentum, and consequently only a single value of the velocity, is possible. These cells, representing the discontinuity of the processes involved, are larger, the smaller the volume in which the gas is enclosed.

CHAPTER IV

THE RELATION BETWEEN WAVE MECHANICS AND THE THEORY OF RELATIVITY

THE fact that de Broglie made the Lorentz Transformation the starting point for his theory shows that there must be a close connection between wave mechanics and the theory of relativity, and leads to the expectation that possibly the fundamental laws of the mechanics of relativity might be derivable from classical mechanics by means of the conception of material waves. It has been shown by the author * that this extension may in fact be made, without ascribing to the material waves any other property beyond the fact that their energy is composed of Planck energy quanta.

For the purpose of this deduction, we start from the idea that the material particles are the energy centres of waves whose group velocities manifest themselves as mechanical velocities. By comparing the two classical principles of Maupertuis and Fermat, we then deduce a universal proportionality between the mechanical velocity (v) and the reciprocal of the wave velocity ($1/u$) ; in other words, we make the product of u and v equal to a universal constant which may be represented by w^2 , so that

$$uv = w^2 \dots \dots \dots \dots \quad (33)$$

v being connected with u in the same way as the quantity g is connected with u in equation (13). We thus find, from equations (13) and (33),

$$\frac{1}{v} = \frac{1}{w^2} \frac{d(v\nu)}{d\nu}$$

* *Phys. Zeitschr.* **28**, (1927), pp. 632-634.

or

$$w^2 dv = v^2 dv + vd \left(\frac{v^2}{2} \right);$$

since w is a constant, we may write this equation in the form

$$\frac{dv}{v} = -\frac{1}{2} \frac{d(w^2 - v^2)}{w^2 - v^2}.$$

By integration of this differential equation, we find

$$\ln v = \ln \frac{1}{\sqrt{w^2 - v^2}} + \ln C,$$

where C is an integration constant. Therefore

$$v = \frac{C}{w \sqrt{1 - \frac{v^2}{w^2}}} \quad \dots \quad (34)$$

Up to the present we have only made use of the hypothesis of material waves. We may now combine with this the quantum hypothesis of Planck, making the product of the frequency and the elementary quantum equal to the energy of a material particle. Introducing the new constant K , given by the equation

$$K = \frac{hC}{w^3} \quad \dots \quad (35)$$

we obtain for the energy of a particle

$$E = \frac{Kw^2}{\sqrt{1 - \frac{v^2}{w^2}}} \quad \dots \quad (36)$$

To aid discussion of this equation, we will first interpolate some brief considerations on the basis of classical mechanics. Let the velocity of a body of mass μ be increased by the addition of an infinitely small velocity, dv , in the direction of motion. Owing to this "longitudinal" increase of velocity, the kinetic energy suffers an increase of $\mu v dv$. Now when a force P_1 , acting in the

direction of motion, produces an acceleration b_1 , Newton's second law of motion gives the relation, $P_1/b_1 = \mu$. We may therefore write the following equation

$$dE = \frac{P_1}{b_1} v dv \quad \dots \dots \quad (37)$$

Differentiation of equation (36) with respect to v gives

$$\frac{dE}{dv} = \frac{Kv}{\left(1 - \frac{v^2}{w^2}\right)^{\frac{3}{2}}} \quad \dots \dots \quad (38)$$

Further, according to Newton's second law, the vector of the force is equal to the differential coefficient of the momentum with respect to time. If we imagine both the force and the momentum resolved into two components, a longitudinal component in the direction of motion and a transverse component perpendicular to it in the plane of motion, we have the following relations for the two components of force

$$P_1 = \frac{d(mv_1)}{dt}, P_2 = \frac{d(mv_2)}{dt},$$

where the suffixes 1 and 2 refer to the longitudinal and transverse components respectively. If, when differentiating, we do not arbitrarily exclude the possibility that the mass may vary with time, we obtain the following equations

$$\left. \begin{aligned} P_1 &= m \frac{dv}{dt} + v \frac{dm}{dt} \\ P_2 &= mb_2 \end{aligned} \right\} \quad \dots \dots \quad (39)$$

since v_2 vanishes * and v_1 is equal to the magnitude of the velocity v . Finally, according to a well-known elementary relation of mechanics, the longitudinal component of the acceleration is equal to the differential coefficient of the velocity with respect to time; that is to say—

$$b_1 = \frac{dv}{dt}.$$

* For the velocity is in the direction of motion.

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If, therefore, we divide the first of equations (39) by b_1 , we obtain, in conjunction with equations (37) and (38)

$$\frac{K}{\left(1 - \frac{v^2}{w^2}\right)^{\frac{3}{2}}} = m + v \frac{dm}{dv} \quad \dots \quad (40)$$

The solution of this differential equation is readily seen to be

$$m = \frac{K}{\sqrt{1 - \frac{v^2}{w^2}}} \quad \dots \quad (41)$$

for then

$$\frac{dm}{dv} = \frac{K \frac{v}{w^2}}{\left(1 - \frac{v^2}{w^2}\right)^{\frac{3}{2}}} = \frac{m \frac{v}{w^2}}{1 - \frac{v^2}{w^2}},$$

and therefore

$$m + v \frac{dm}{dv} = \frac{m}{1 - \frac{v^2}{w^2}},$$

in agreement with equations (40) and (41).

If, in equation (41), we put $v = 0$, we obtain

$$m_0 = K \quad \dots \quad (42)$$

the constant K therefore represents the “*stationary mass*.” Again, in the special case where u and v coincide, v will, according to equation (33), be equal to w , and therefore, from equation (41), the mass will be infinite so long as the stationary mass is greater than zero. Conversely, at a velocity w , the mass (and therefore according to equation (36) the energy) can only remain finite when the stationary mass vanishes. On these grounds we may well identify w with velocity of propagation of the light quanta, which though “imponderable” are none the less capable of exhibiting the effects of momentum. Thus, by setting w

equal to the velocity of light c , and remembering equation (42), we may write equation (41) in the form

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad \dots \quad (43)$$

This equation, however, is nothing more than the well-known mass equation of the theory of relativity, which expresses the mass as a function of the velocity. We can also see from equation (43) that a body possessing a stationary mass greater than zero can never attain a mechanical velocity equal to that of light. Comparison of equations (37) and (38), in conjunction with equation (42), gives the well-known relativity formula for the longitudinal mass (the quotient P_1/b_1), *i.e.*,

$$m_{long} = \frac{m_0}{\left(1 - \frac{v^2}{c^2}\right)^{\frac{3}{2}}} \quad \dots \quad (44)$$

On the other hand, the second of equations (39), together with equation (43), gives the following value for the transversal mass (P_2/b_2)

$$m_{trans} = \frac{m_0}{\left(1 - \frac{v^2}{c^2}\right)^{\frac{1}{2}}} \quad \dots \quad (45)$$

again in accordance with the theory of relativity.

Finally, since $w = c$, comparison of equations (36) and (41) gives

$$E = mc^2 \quad \dots \quad (46)$$

or the fundamental relativistic law of the inertia of energy.

CHAPTER V

THE DIFFRACTION OF MATERIAL WAVES

THE theory of de Broglie leads of necessity to the conclusion that moving particles of matter can be deflected by other particles in the vicinity. Thus, when the path of an atom, or a molecule, or a free electron passes so close to an obstacle that the separation is of the order of magnitude of the corresponding de Broglie wave, a bending of the material wave must evidently occur, and therefore deviations from the classical laws of motion must arise. Einstein * and Elsasser † were the first to draw this most important conclusion from de Broglie's theory. From the fundamental relation given by de Broglie's theory for the connection between the wavelength and the momentum (equation (18)) it follows that the wavelength corresponding to an electron which moves at one hundredth of the velocity of light is about 10^{-8} cm., and that for a proton moving with a velocity corresponding to that of a gas molecule at room temperature, the wavelength is approximately of the same magnitude. In proportion as the velocity becomes lower, the de Broglie wavelength increases, and appreciable diffraction effects for material waves are therefore to be expected particularly in the case of slow-moving electrons and at very low temperatures.

As a matter of fact, Einstein has already attempted to explain in this way the important deviations from their usual laws exhibited even by perfect gases at the very lowest temperatures. These phenomena—the so-called "gas degradation"—were ascribed by Einstein to the fact that at a certain very low range of temperatures the

* *Sitz.-Ber. Berliner Akad. d. Wiss., math. nat. Klasse*, 1925, p. 9.

† *Naturwissenschaften*, 1925, p. 711.

wavelength of the material waves becomes of the same order of magnitude as the molecular diameter. The experiments of Günther * are also in agreement with this hypothesis. This investigator, at the suggestion of Nernst, examined the viscosity (internal friction) of hydrogen at very low temperatures, and demonstrated the occurrence of a sudden acceleration in the fall of viscosity on reaching a critical temperature range.

Elsasser completed the above-mentioned idea of Einstein by drawing attention to the probability of diffraction effects during collisions between free electrons and atoms. The passage of free electrons through gases had already been thoroughly investigated by many experimenters, in particular by Ramsauer.†. In this connection, Ramsauer made the puzzling discovery that in some of the inert gases ‡ the mean free path of the electrons increases with decrease of velocity in such a way that the slow moving electrons appear to pass almost without opposition through the atoms. Elsasser drew attention to the fact that the mysterious "Ramsauer effect" should evidently be ascribed to diffraction of the material waves associated with the electrons, since slow moving electrons appear to be scattered by the atoms according to the same law as that which governs the scattering of light waves, of wavelength equal to that of the corresponding material waves, by spheres of radii equal to those of the atoms.

Elsasser's hypothesis later obtained satisfactory confirmation by the experiments of Dymond § on the scattering of electrons during their passage through helium gas. Dymond investigated the relation between the scattering angle and the number of electrons scattered in a given direction. If Elsasser's theory is correct, the intensity

* *Zeitschr. f. physik. Chem.* **110**, 1924, p. 626.

† *Ann. d. Physik.* **72**, 1923, p. 345; see also the summary of Minkowski and Sponer in "Ergebnissen der exakten Naturwissenschaft," Vol. 3 (Springer, Berlin, 1924).

‡ In the chemically inert gases the atoms have no affinity for electrons.

§ *Nature*, **118**, 1926, pp. 336-337.

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of the scattered material waves must naturally vary with the direction, showing maxima and minima of intensity in just the same way as a screen on which diffracted light falls exhibits alternate bright and dark strips. Where for a given angle the intensity of the material waves is a maximum, there also must the measured deviation of the electrons be a maximum.

In his experiments, Dymond cut off by means of two narrow slits a narrow beam from the electrons emitted by an incandescent tungsten wire. This beam he passed through helium gas at a very low pressure (0.03 mm.). Two other slits enabled the electrons scattered in any given direction to be isolated. The tungsten wire and the two first slits could be turned, and in this way Dymond was able to give the angle of scattering any desired value between 0° and 90°. By this means he actually succeeded in finding two fairly sharply defined maxima for two definite angles (whose value depended on the voltage *).

As far back as 1923, Davisson and Kunzman † had found signs of similar phenomena in the reflection of slow moving electrons at metal surfaces, and Elsasser was the first to point out that the results of these experiments might probably be regarded as supporting de Broglie's theory. In 1927, Davisson, in collaboration with Germer, ‡ carried out similar experiments with crystals, and succeeded by means of these experiments in bringing for-

* Dymond investigated the diffraction for the case of so-called inelastic collision between helium atoms and electrons, in which the electrons lose just so much energy as is necessary to transfer a helium atom from the normal state into the next higher state. Such collisions produce a diminution in the energy of the electrons corresponding to a drop of 20 volts. With an initial velocity corresponding to 100 volts, Dymond found two maxima, a sharp one at 5° and a broader at 60°. On diminishing the voltage to 50, the angle of the sharp maximum diminishes to 20°. Increasing the voltage above 100 on the other hand again diminishes the angle at which the maximum occurs. In addition to the maxima described, a third appears at potentials above 200 volts; the position of this third maximum is independent of the velocity, i.e., the voltage, and the reason for its presence is not yet explained.

† *Physical Review*, 22, 1923, p. 243.

‡ *Nature*, 119, 1927, p. 558. More complete description in *Physical Review*, 30, 1927, p. 705.

ward the most satisfactory confirmation so far obtained of the hypothesis of material waves. It was shown, in fact, that electrons, on striking a crystal surface, are deflected by the crystal just in the same way as X-rays.

The method adopted was to direct a narrow beam of electrons normally upon a small plate cut from a single crystal of nickel, and to measure with a galvanometer the intensity of the scattered electrons at various angles. Sharply defined maxima were found in definite directions, and a close connection was found between these directions and those in which X-rays were reflected from the crystal in accordance with the known laws.* Thus, if the known structure of the nickel crystal is assumed to be contracted in the direction parallel to the primary electron beam in a ratio lying between $0.7 : 1$ and $0.9 : 1$, it is found that the maxima of the electron scattering coincide exactly with the directions in which the X-rays would then be reflected. If, on the other hand, the wavelengths of the material waves associated with the process, are calculated from the diffraction phenomena, they are actually found (in agreement with equation (18)) to be equal to the elementary quantum divided by the product of mass and velocity.

The experiments of G. P. Thomson † form an important corollary to the work of Davisson and Germer. Thomson allowed rapidly moving electrons of 20,000 to 30,000 volts, *i.e.*, of a wavelength of about 10^{-9} cm., to fall on very thin foil of gold and other metals. The same phenomena occurred as had previously been observed by Debye and Scherrer when X-rays were allowed to impinge on metal foil. In Thomson's experiments the characteristic diffraction rings of Debye and Scherrer were again formed on a photographic plate set up behind the foil. From the rings, Thomson was able to calculate lattice con-

* It is well known that, in reflecting an incident beam of X-rays, a crystal isolates rays of definite wavelengths.

† G. P. Thomson, *Proc. Roy. Soc.* **117**, (A), 1928, p. 600.

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stants which had the same values as those previously known from the X-ray exposures.

In contrast to Thomson, whose electron beam corresponded to very hard X-rays, Rupp* obtained very beautiful diffraction phenomena with slow moving electrons passed through extremely thin foil. In his experiments he used Cole's † discovery, that slow moving electrons (of about 30 volts) will blacken the ordinary photographic plate,‡ and also a remarkable discovery of Becker,§ who proved that metal foil is selectively penetrated by electrons with a definite range of velocities.

* E. Rupp, *Ann. d. Phys.* **85**, 1928, p. 981.

† K. Cole, *Phys. Rev.* **28**, 1926, p. 781.

‡ The sensitivity of plates to the action of the electrons can be appreciably increased by sensitisation with oil.

§ A. Becker, *Ann. d. Phys.* **84**, 1927, p. 778.

CHAPTER VI

SCHRÖDINGER'S THEORY

THE ideas of de Broglie appear to have established a close connection between mechanical processes and the general principles of wave propagation, which have been formulated most clearly for optical phenomena. The fundamental equations of traditional mechanics were reduced by de Broglie to Fermat's Principle, which, in its special application to optically homogeneous media, postulates the rectilinear propagation of light.* It is, however, known that the assumption of rectilinear propagation of light in homogeneous media is by no means exactly true, since it is contradicted by the actually observed optical phenomena of diffraction. The assumption itself, and with it Fermat's Principle, is only accurate so long as it is restricted to distances which are large in relation to the wavelength of light.

When this is not the case, the propagation of light must be considered on the basis of a principle established in the second half of the seventeenth century by Huygens, and called after him, Huygens' Principle. Essentially, this principle says that any point which is reached by a light wave itself becomes in turn the origin of new elementary waves which spread out from it in all directions with the velocity of the original wave.

The exact mathematical expression of Huygens' principle may be given in the form of a relatively simple differential equation connecting the so-called Laplace

* If the wave velocity is assumed in equation (1) to be constant, the equation shows that the total path of the ray must be a minimum, and therefore a straight line, since this is the shortest path between the two points.

derivative of a physical quantity with its second differential coefficient with respect to time. The Laplace operator, usually represented* by the symbol Δ , when applied to a function S , gives the following expression, which is the sum of the second partial differential coefficients along the three co-ordinates, of which co-ordinates its value is independent :

$$\Delta S = \frac{\partial^2 S}{\partial x^2} + \frac{\partial^2 S}{\partial y^2} + \frac{\partial^2 S}{\partial z^2} \quad \dots \quad (47)$$

In the particular case where the quantity S has the property that its Laplace derivative is proportional to its second differential coefficient with respect to time, *i.e.*, when

$$\frac{\partial^2 S}{\partial t^2} = \kappa \Delta S \quad \dots \quad (48)$$

it is shown in theoretical physics, as is well known,† that an undulatory propagation of the quantity S is possible, the process occurring with a wave velocity.

$$u = \sqrt{\kappa} \quad \dots \quad (49)$$

In addition, it follows from equation (48) that any point at which a disturbance occurs due to the wave will itself be the starting point of a new elementary wave, which will travel with the same velocity u , and will form spherical waves in a homogeneous medium.

Now the phase depends upon the time, irrespective of whether plane or spherical waves are being considered, as given, according to equation (6), by the simple relation

$$\frac{\partial \phi}{\partial t} = 2\pi\nu.$$

Therefore, in the particular case where the waves are of pure sine form, since in that case S is equal to the ampli-

* Instead of the symbol ΔS , the symbol $\nabla^2 S$ is also often used.

† See, for example, "Introduction to Theoretical Physics," by the author, second English edition (Constable, London, and Van Nostrand, New York, 1928), Vol. I., § 43.

tude multiplied by the sine of the phase angle, and since two differentiations of the sine give the sine once more (but negative instead of positive), we obtain

$$\frac{\partial^2 S}{\partial t^2} = A \frac{\partial^2 (\sin \phi)}{\partial t^2} = -4\pi^2 v^2 A \sin \phi = -4\pi^2 v^2 S.$$

From this relation and equation (49), equation (48) may therefore, in the case of sine waves, be expressed in the form

$$4S + \frac{4\pi^2 v^2}{u^2} S = 0 \quad \dots \quad (50)$$

Now it was Schrödinger's ingenious idea to attempt a generalisation of mechanics which should be analogous to the transition from Fermat's to Huygens' principle, that is, from the geometrical optics of rays to the physical optics of waves. Such a transition is, as a matter of fact, suggested by the phenomena described in the previous chapter on the diffraction of material waves.

The transformation becomes particularly simple when a single particle is considered, since then, from de Broglie's relation between wavelength and momentum (equation (20))

$$\frac{v^2}{u^2} = \frac{m^2 v^2}{h^2} \quad \dots \quad (51)$$

Further, the kinetic energy ($1/2 mv^2$) is equal to the difference between the total energy (E) and the potential energy (V). Therefore, from equation (51), equation (50) may also be written in the form

$$4S + \frac{8\pi^2 m}{h^2} (E - V) S = 0 \quad \dots \quad (52)$$

This differential equation forms the basis of Schrödinger's mechanics.

Now, from the theory of differential equations, it has long been known that the possibility of finding a general finite and continuous solution to a differential equation

exists only for definite values of the parameters occurring in the equation. The particular values for which this possibility is realised are known as the characteristic values of the differential equation, and the solutions corresponding to them as the characteristic functions. In Schrödinger's equation, the total energy E appears as a constant parameter, while the potential energy naturally depends on the co-ordinates. The characteristic values of Schrödinger's equation in any particular case, therefore represent quite definite discrete values of the energy. The physical problem of the quantisation of energy thus appears to have been reduced by Schrödinger to a purely mathematical problem, namely, to that, long since solved for all the most important cases, of the characteristic values of differential equations.

The mathematical problem of characteristic values may be explained briefly, and without going into minor details, by two simple examples, which will be of significance in the later discussion. Let us consider first the function

$$y = e^{-\frac{x^2}{2}} \dots \dots \dots \quad (53)$$

and find the first and second differential coefficients with respect to x ; let them be represented by y' and y'' . We have then

$$y' = -xy,$$

and by a second differentiation

$$y'' = -y - xy',$$

or, from the last equation but one,

$$y'' = y(-1 + x^2).$$

If then we consider the differential equation

$$\frac{d^2y}{dx^2} + (a - x^2)y = 0 \dots \dots \dots \quad (54)$$

we see that this equation has a solution of the form of equation (53) as long as the parameter a has the value of

unity. The number 1 thus represents a characteristic value of the differential equation.

We obtain another characteristic value by writing

$$y = 2xe^{-\frac{x^2}{2}} \dots \dots \dots \quad (55)$$

and we then find

$$y' = 2e^{-\frac{x^2}{2}} + 2xe^{-\frac{x^2}{2}}(-x) = 2e^{-\frac{x^2}{2}}(1-x^2).$$

From this, by further differentiation, it follows that

$$y'' = 2e^{-\frac{x^2}{2}}(1-x^2)(-x) + 2e^{-\frac{x^2}{2}}(-2x);$$

therefore, from equation (55)

$$y'' = y(-3+x^2).$$

Thus, the value $a = 3$ is another characteristic value for the differential equation (54), and equation (55) is the corresponding solution.

The subsequent solutions will only be briefly mentioned here, since the reader may easily satisfy himself by calculation. They may be expressed in the form

$$y = He^{-\frac{x^2}{2}},$$

where H , which is equal to 1 and $2x$ for the characteristic values 1 and 3, has the following values

$$H = 4x^2 - 2 \quad \text{for } a = 5$$

$$H = 8x^3 - 12x \quad \text{for } a = 7$$

$$H = 16x^4 - 48x^2 + 12 \quad \text{for } a = 9, \text{ etc.}$$

The five values given here are the five lowest terms in the so-called Hermitean Polynomial, which may be constructed from a simple formula.*

The Hermitean polynomials multiplied by $e^{-\frac{x^2}{2}}$ give the

* The Hermitean polynomial corresponding to the characteristic value $a = 2n + 1$ has the form

$$\begin{aligned} H &= (2x)^n - \frac{n(n-1)}{1} (2x)^{n-2} \\ &+ \frac{n(n-1)(n-2)(n-3)}{1 \cdot 2} (2x)^{n-4} \dots \dots \end{aligned}$$

The series comes to an end before the term for which one of the factors becomes for the first time equal to zero.

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solutions of the differential equation (54) for which the odd whole numbers form the characteristic values. For the rather complicated proof that the differential equation has no other solutions than the above, reference must be made to comprehensive mathematical works.*

As a further example, a short consideration of the so-called spherical functions may be given. The differential equation of these functions is obtained by transforming the Laplace derivative from rectangular to three-dimensional polar co-ordinates. These co-ordinates, as is well known, are the distance (r) from a fixed point, and two angles corresponding on the earth to the geographical longitude and the complement of the geographical latitude. The transformation leads to an expression which may be denoted by the symbol Δ^* for the particular case where r is constant and equal to 1.†

The differential equation of the spherical functions is thus

$$\Delta^* \psi + a\psi = 0 \quad \dots \quad (56)$$

and it follows from the theory of spherical functions, ‡ which will not be discussed further here, that this differential function can only have a continuous finite solution other than zero over the whole sphere (with its first derivatives) when an integral value for n is placed in the equation

$$a = n(n + 1) \quad \dots \quad (57)$$

The numbers 2, 6, 12, 20, 30, 42, 56, etc., are therefore the characteristic values of the differential equation (56).

* See, for example, Courant and Hilbert, *Methoden der mathematischen Physik*, Vol. I., Berlin (Springer), 1924, p. 261.

† If ϕ corresponds to the geographical latitude and θ to the polar distance,

$$\Delta^* \psi = \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 \psi}{\partial \phi^2}.$$

‡ See, for example, Courant-Hilbert, Vol. I., pp. 264-266 and 422.

CHAPTER VII

THE MECHANICS OF CHARACTERISTIC VALUES. EXAMPLES

SCHRÖDINGER's method, which reduces the problem of quantisation to a question of characteristic values, may now be applied to the simple case of an oscillator. By an oscillator is meant a particle, *e.g.*, an electron, which vibrates about a fixed position of rest. The oscillator is described as linear when the vibrations occur in a straight line, and as harmonic when they are purely sinusoidal. The quantum theory had its starting point in 1900 in the consideration of a linear, harmonic oscillator, and for a quarter of a century theoretical physicists have adhered to the result thus obtained by Planck, that the energy of such an oscillator is always an integral multiple of the product of the frequency and the elementary quantum. Schrödinger's theory, however, leads to a different result.

If the position of rest of the oscillator is chosen as the origin of a system of co-ordinates, the straight line in which the vibrations occur being the x -axis, the following relation naturally holds

$$x = A \sin (2\pi\nu t),$$

where A is the amplitude. The velocity, being the differential coefficient of the distance x with respect to time, amounts to

$$v = A \cdot 2\pi\nu \cos (2\pi\nu t).$$

The kinetic energy is half the product of the mass and the square of the velocity, and is therefore

$$L = 2A^2\pi^2\nu^2m \cos^2 (2\pi\nu t).$$

We may obtain the total energy E from this equation by putting the cosine equal to 1, for as the particle passes its

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point of rest the potential energy is zero, and the greatest possible value of the kinetic energy then represents the total energy. Since the sum of the squares of sine and cosine is equal to 1, the expression for the potential energy V is obtained by replacing the cosine by the sine in the last equation. In conjunction with the last equation but two this gives

$$V = 2\pi^2\nu^2mx^2.$$

For the special case under consideration, that of a linear harmonic oscillator, Schrödinger's differential equation assumes the form

$$\frac{\partial^2 S}{\partial x^2} + \frac{8\pi^2m}{\hbar^2} (E - 2\pi^2\nu^2mx^2)S = 0,$$

since the Laplace derivative ΔS reduces to the second derivative with respect to x .

For the sake of brevity we may now write

$$\frac{8\pi^2m}{\hbar^2}E = \alpha$$

and

$$\frac{4\pi^2m\nu}{\hbar} = \beta.$$

Further, we may introduce a new variable ξ by the definition

$$\xi = x\sqrt{\beta}.$$

We then obtain

$$\frac{\partial^2 S}{\partial x^2} = \beta \frac{\partial^2 S}{\partial \xi^2}$$

and

$$x^2 = \frac{\xi^2}{\beta}.$$

Dividing the differential equation by β , we obtain

$$\frac{\partial^2 S}{\partial \xi^2} + \left(\frac{\alpha}{\beta} - \xi^2\right) S = 0.$$

According to the principles laid down in the previous

chapter, the characteristic values of this equation are determined by the relation

$$\frac{\alpha}{\beta} = 2n + 1,$$

where n has integral values. Therefore, from the definitions of α and β

$$E = (2n + 1) \frac{h\nu}{2} \quad (58)$$

In Schrödinger's mechanics the energy of a linear harmonic oscillator is accordingly given as an odd multiple of a half quantum element, thus

$$\frac{h\nu}{2}, \frac{3h\nu}{2}, \frac{5h\nu}{2}, \text{etc.}$$

This is in disagreement with the earlier quantum theory, which gave the energy as always a multiple of a whole quantum (*i.e.*, as 0, $h\nu$, $2h\nu$, $3h\nu$, etc.). In contradiction to the older theory, it follows from Schrödinger's theory that the smallest energy content which an oscillator can possess is greater than zero. Now physical theory ascribes the heat content of solid bodies to vibrations executed by the atoms comprising those bodies about fixed positions of rest; it is the energy of these oscillators which manifests itself as heat. Various discrepancies between the older quantum theory and certain of the phenomena observed at extremely low temperatures led some physicists, Nernst in particular, to the hypothesis of the so-called zero point energy. According to this hypothesis, even at the absolute zero of temperature, where according to the earlier theory the energy of oscillation must vanish completely, each oscillator must possess the energy $h\nu/2$. This assumption, which at first appeared somewhat forced, is now seen to be a necessary consequence of the fundamental principles of Schrödinger's mechanics.

Besides the oscillator, another instance of the application of Schrödinger's mechanics may be considered, which was also thoroughly worked out on the older quantum

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theory. This is the case of a particle moving at a constant distance round a fixed centre, the so-called rotator. If the motion is confined to one plane, the path becomes a circle, and we then speak of a rotator with fixed axis. If, on the other hand, the motion is not so limited, the path lying on the surface of a sphere, we speak of a rotator with free axis. This second kind of motion will be considered in the following discussion.

When the fixed distance is equal to unit length, we may replace the Laplace operator in Schrödinger's differential equation by the symbol Δ^* , already used in the previous chapter. When the radius of the path is r we must, of course, divide this expression by r^2 , since the Laplace derivative contains the square of the differentials of the co-ordinates in the numerator. In this case, therefore, ΔS must be replaced by $\Delta^* S/r^2$. The potential energy, and consequently the kinetic energy also, are constant in the case of a revolving particle. If, therefore, we denote the kinetic energy by L , Schrödinger's equation (after multiplication by r^2) may be written in the form

$$\Delta^* S + \frac{8\pi^2 m}{h^2} r^2 LS = 0 \dots \dots \quad (59)$$

According to what has been said in the previous chapter, however, on the differential equation of spherical functions (equation (56)), we know that the last equation only has a solution when, for integral values of n

$$\frac{8\pi^2 m r^2 L}{h^2} = n(n+1) \dots \dots \quad (60)$$

In this equation it is convenient to introduce the angular momentum, U , which is defined as the product of the mass, velocity and orbital radius, thus

$$U = mvr.$$

Since, also, the kinetic energy is $\frac{1}{2}mv^2$,

$$mr^2 L = \frac{1}{2} U^2.$$

According, therefore, to equation (60)

$$\frac{4\pi^2 U^2}{h^2} = n(n+1),$$

or,

$$U = \frac{h}{2\pi} \sqrt{n(n+1)} \quad \dots \quad (61)$$

It will be seen, therefore, that, in the case of the rotating particle also, Schrödinger's theory leads to results at variance with the older quantum theory. The latter gave the value $nh/2\pi$ for the angular momentum, or values of 0, 1, 2, 3, 4, etc. for $2\pi U/h$. Schrödinger's theory, on the other hand, gives, instead of integral numbers, the values

$$0; 1.4142; 2.4495; 3.4641; 4.4721, \text{ etc.}$$

for $2\pi U/h$.

In this case also, Schrödinger's theory is in better agreement with experiment than the earlier theory (especially in the explanation of band spectra). The variation again consists essentially in the introduction of half quantum numbers.* On account of the constancy of the potential energy, it follows from equation (60) that the difference between any two given values of the energy is represented by the equation

$$E_1 - E_2 = \frac{h^2}{8\pi^2 mr^2} [n_1(n_1+1) - n_2(n_2+1)].$$

Since, however,

$$n(n+1) = \left(n + \frac{1}{2}\right)^2 - \frac{1}{4},$$

it follows that

$$E_1 - E_2 = \frac{h^2}{8\pi^2 mr^2} \left[\left(n_1 + \frac{1}{2}\right)^2 - \left(n_2 + \frac{1}{2}\right)^2 \right].$$

The application of the mechanics of characteristic

* Half quantum numbers were, in fact, already used in the theory of band spectra, although no satisfactory theoretical grounds could be adduced.

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values to the hydrogen atom leads to a very remarkable result. The hydrogen atom consists of a proton with an electron revolving round it. The potential energy in this case is

$$V = -\frac{e^2}{r},$$

where e is the elementary quantum of electricity, and r the distance between proton and electron. For the case of the hydrogen atom, Schrödinger's differential equation therefore assumes the form

$$\Delta S + \frac{8\pi^2 m}{h^2} \left(E + \frac{e^2}{r} \right) S = 0 \quad \dots \quad (62)$$

The calculation of the characteristic values of this equation is exceedingly complicated, and reference must therefore be made to Schrödinger's original paper.* Schrödinger found that the characteristic values of the differential equation might be represented by any positive number, but only by certain definite negative numbers. The energy, E , can assume any given positive value, but only such negative values as satisfy the equation

$$E_n = -\frac{2\pi^2 me^4}{h^2 n^2} \quad \dots \quad (63)$$

for integral values of n .

The energy values of the hydrogen atom determined by equation (63) are in complete agreement with those found by Bohr in 1913, which are, as shown by the formula, inversely proportional to the squares of the principal quantum numbers. Further, as has been already mentioned, values identical with those of Bohr are also obtained by application of the original de Broglie hypothesis of material waves to periodic motion in a closed orbit. Unlike motions which have negative energy values, motions with positive energy values are not quantised.

* *Ann. d. Phys.* **79** (1926), pp. 361-376.

This deduction agrees with the results of the older quantum theory, which, while postulating definite particular elliptical (or, under some circumstances, circular) orbits, introduced no quantum limitations for the case of the open hyperbolic paths described by electrons approaching a nucleus from outside and again receding from it.*

Another important application of Schrödinger's differential equation in its simplest form (equation (52)) may be made in the case where the motion of an electron is disturbed by relatively weak outside influences, by an external electric field, for example. It follows from the theory of differential equations that the characteristic values of an equation, and the characteristic functions corresponding to them (the corresponding solutions), assume only slightly different values when a sufficiently small perturbing term is introduced into the equation. This fact makes it possible to calculate, from the known characteristic quantities of the original equation, the alterations which will occur when the perturbing term is added. If, for example, a_k is a characteristic value of the "unperturbed" equation, it is possible to determine the amount a_k by which the corresponding characteristic value of the "perturbed" equation will differ from a_k .

Now, if the differential equation contains several variables, independent of one another, as is the case, for example, in Schrödinger's equation (except in special circumstances), then to each characteristic value there are a number of corresponding solutions, or, in other words, a number of characteristic functions. If the number of these is s , we may speak of an s -fold characteristic value, or we may also say that s characteristic values coincide. The significant result of this mathematical

* For every distance of separation from the nucleus there is a definite corresponding critical velocity for which the path is a parabola; for smaller velocities the orbit is an ellipse, for larger velocities it is a hyperbola. This is in agreement with the known laws of celestial mechanics, which assume hyperbolic paths in the case of comets. The critical velocity of an electron, like that of a comet, is determined by the square root of $\frac{2 \times \text{potential energy}}{\text{mass}}$.

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consideration is that, when the equation is "perturbed," the alterations a_k corresponding to coincident characteristic values will not themselves be identical, since they also depend on the characteristic functions, which differ among themselves. Thus, when a multiple characteristic value is "perturbed," it may be replaced by a group of different characteristic values which are adjacent to one another and to the original characteristic value. The latter is said to be resolved, either completely (*i.e.*, into s components) or partially.

The development of this principle and its application to the motion of an electron in an electric field led Schrödinger to a formula which is in agreement with one already developed by Epstein in 1916. In accordance with the experimental results, this formula leads to a resolution of the energy values, and hence also of the spectral lines, in an electric field; it leads, that is to say, to a prediction of the so-called Stark effect. The following formula for the alteration of energy in an electric field is obtained

$$\Delta E = \frac{3}{8\pi^2} \frac{\hbar^2 F}{me} n(k_2 - k_1) \dots \dots \quad (64)$$

where F is the field strength, n the "principal quantum number," and k_1 and k_2 two other integral quantum numbers whose sum must be at least one less than the principal quantum number.

The problems considered so far have dealt with a single electron. For the treatment of processes in which more than a single particle is concerned, Schrödinger's equation assumes a more general form. If we designate by Δ_1 the sum of the second partial differential coefficients with respect to the co-ordinates of the first particle, and by m_1 its mass, etc., the generalised Schrödinger equation, as will be more fully established in a later chapter (see equation (122)), becomes

$$\frac{1}{m_1} \Delta_1 S + \frac{1}{m_2} \Delta_2 S + \dots + \frac{8\pi^2}{\hbar^2} (E - V) S = 0 \quad (65)$$

It must, however, be borne in mind that this equation is not an actual wave equation in the ordinary sense. The process which it represents can only be regarded as a "wave" in a $3n$ -dimensional configuration space, where n is the number of particles taking part, and where the co-ordinates have the meaning of length multiplied by the square root of the mass of the corresponding particle.* The analogy between light waves in three-dimensional space and the material waves thus appears in Schrödinger's theory to be limited to the special case of the single electron.†

* The complication of co-ordinates having the dimensions
length $\times \sqrt{\text{mass}}$
may be avoided when all the particles have the same mass.

† For an explanation of Schrödinger's field scalar S , see Chapter XI.

CHAPTER VIII

THE QUANTUM MECHANICS OF HEISENBERG

THE development of Schrödinger's theory on the ideas of de Broglie is not the only attempt to found a new conception of atomic physics. It was anticipated by some months by the quantum mechanics of Heisenberg, though, as Schrödinger was able to show, the ideas of Heisenberg stand in the closest relationship to his own theories. This is the more remarkable, since Heisenberg, in developing his theory, had in view a goal quite different from that of de Broglie and Schrödinger. These two investigators started with the aim of depicting atomic phenomena in terms of classical physics, so as to bridge the gulf between "quantised" atomic physics and classical mechanics. Heisenberg, on the other hand, started with the opposite point of view, that only a complete renunciation of classical principles could give a true picture of atomic laws. Heisenberg was convinced that any attempt at forming a definite visual picture of the processes of atomic physics was useless and unreasonable, and should be abandoned at the outset, and that, above all, every quantity should be excluded from atomic theory which is not susceptible to direct observation.

Instead of the earlier quantum theories, which were based on the investigation of unverifiable assumptions of electronic orbits, Heisenberg therefore sought to develop a new quantum mechanics which should contain only relations between the observable magnitudes of atomic physics. The only such magnitudes chosen by Heisenberg were the frequency and intensity of the spectral lines characteristic of the atoms, together with such information about the energy levels of the atom as could be deter-

mined from non-spectroscopic data such as experiments on electron impacts. The aim of the new quantum mechanics, as envisaged by Heisenberg, was, first, to build up, from spectroscopic data, magnitudes which could be used for purposes of calculation in place of the co-ordinates and velocities of electrons ; and subsequently to deduce relationships between these magnitudes, in as close agreement as possible with the established models of classical mechanics, which should permit of a deduction of rules of quantisation nearer, if possible, to the facts, and of greater applicability than the earlier theory.

The method adopted by Heisenberg for carrying out this programme took as its starting point a theorem propounded by Fourier at the beginning of the nineteenth century. Fourier had shown that any given periodically varying quantity may be represented by the sum of a number of pure sine curves, each of which can be written as in equation (3), in the form

$$q_n = A_n \sin (2\pi\nu_n t + \epsilon_n) \dots \dots \quad (66)$$

where A represents the amplitudes and ϵ the phase constants. (In parenthesis it may be remarked that the frequencies ν_n are all integral multiples of the fundamental frequency at which the quantity under consideration is varying, and that the values of A_n may be calculated from the functional relations between the quantity concerned and the time *.) The periodic variations of the quantity under consideration may thus be replaced by the sum of the partial vibrations

$$q_1, q_2, q_3 \dots$$

For the following discussion it is convenient to represent

* Thus, if $\phi(x)$ is the periodic function, we may write

$$\phi(x) = \sum_n a_n \sin (nx) + \frac{1}{2}b_0 + \sum_n b_n \cos (nx).$$

Calculation then gives

$$a_n = \frac{1}{\pi} \int_{-\pi}^{+\pi} \phi(x) \sin (nx) dx, \quad b_n = \frac{1}{\pi} \int_{-\pi}^{+\pi} \phi(x) \cos (nx) dx.$$

the vibrations by exponential instead of trigonometric functions. For this purpose we may use the well-known formula of de Moivre, according to which

$$e^{ix} = \cos x + i \sin x,$$

where i represents the imaginary quantity $\sqrt{-1}$. By means of de Moivre's formula the real and imaginary parts (in the latter the factor i may be omitted) may be separated from an exponential function with an imaginary exponent, so that the expression may be considered as equating, on the one hand the real, and on the other the imaginary parts. By applying this artifice, well known in theoretical optics, we may represent any vibration in the form

$$S = Ae^{i(2\pi\nu t + \epsilon)} \quad \dots \quad (67)$$

Considering only the imaginary part, we obtain

$$S = A \sin(2\pi\nu t + \epsilon),$$

and it is then seen that the expression obtained by differentiation of equation (67) (again taking only the imaginary part)

$$\frac{dS}{dt} = 2\pi\nu A e^{i(2\pi\nu t + \epsilon)}$$

is equivalent to that obtained directly from the last equation but one, namely,

$$\frac{dS}{dt} = 2\pi\nu A \cos(2\pi\nu t + \epsilon).$$

Applying de Moivre's formula we therefore obtain a very simple relationship between a periodically varying quantity and its differential coefficient with respect to time, namely,

$$\frac{dS}{dt} = 2\pi\nu S \quad \dots \quad (68)$$

Finally, for the sake of brevity, we may write

$$Ae^{i\epsilon} = a \quad \dots \quad (69)$$

so that by the introduction of a complex amplitude a the

inclusion of a phase constant ϵ is rendered superfluous. Equation (67) may then be written in the form

$$S = ae^{2\pi i \nu t},$$

The intensity of the vibrations is given by the square of the real amplitude, *i.e.*, by

$$A^2 = |a|^2 = aa^*,$$

where, as usual, a^* represents the quantity conjugate[†] to a , *i.e.*, in our case (according to equation (69))

$$a^* = Ae^{-i\epsilon}.$$

Now it was Heisenberg's happy idea to replace the periodically variable co-ordinates of the electrons by a system of partial vibrations whose frequencies should coincide with the frequencies of those spectral lines which, according to the earlier conception, could be produced by the electrons during changes in the values of their co-ordinates. Since each frequency in the spectrum corresponds to a transition between two atomic states, it is evident that the partial vibrations belonging to a single electron must form a two dimensional manifold, and can therefore (unlike the Fourier series) be represented by a square array, somewhat according to that shown below, where the numbering is started with zero, corresponding to the normal state

$$\begin{array}{ccccccc} q_{00} & q_{01} & q_{02} & q_{03} & \dots & & \\ q_{10} & q_{11} & q_{12} & q_{13} & \dots & \dots & \dots \\ q_{20} & q_{21} & q_{22} & q_{23} & \dots & & \\ q_{30} & q_{31} & q_{32} & q_{33} & \dots & & \end{array} \quad (70)$$

In future, it will be convenient to write the indices in brackets, thus $q(n, m)$, instead of below the line. In the above expression, then, we must write

$$q(n, m) = a(n, m)e^{2\pi i \nu(n, m)t}. \quad \dots \quad (71)$$

[†] The conjugate quantity to the complex term $x + iy$ is $x - iy$. The magnitude of the two quantities is the same, namely the square root of their product, *i.e.*, $\sqrt{x^2 + y^2}$.

The quantity $a(n, m)$ again represents a complex amplitude, whose value may serve as a measure of the probability of a transition between the n th and m th state; the square of its value therefore determines the intensity of the spectral line emitted during the transition. The probability of a transition must be the same in either direction, and the magnitude of $a(n, m)$ must therefore be equal to that of $a(m, n)$. It is consequently reasonable to regard the two complex amplitudes as conjugate to one another, so that

$$a(m, n) = a^*(n, m).$$

If we further postulate that

$$q(m, n) = q^*(n, m) \quad \dots \dots \dots \quad (72)$$

we see from equation (71) that

$$\nu(m, n) = -\nu(n, m) \quad \dots \dots \dots \quad (73)$$

and, in particular, that

$$\nu(n, n) = 0 \quad \dots \dots \dots \dots \quad (74)$$

Now, if the electron co-ordinates q correspond with the scheme (70), we may arrange the electron velocities \dot{q} in an analogous array in which the individual terms correspond with the differential coefficients (with respect to time) of the members of the first array. We may therefore write

$$\dot{q}(n, m) = 2\pi i \nu(n, m) q(n, m) \quad \dots \dots \quad (75)$$

By differentiating the members of this array once more with respect to time, we may by means of the resulting array obtain an expression for any component (\ddot{q}) of the electron acceleration, so that the following relation is found

$$\ddot{q}(n, m) = -4\pi^2 \nu^2(n, m) q(n, m) \quad \dots \dots \quad (76)$$

From equation (75) we may draw an important conclusion for the special case that in an array

$$q(n, m) = 0 \text{ when } m \neq n \quad \dots \dots \dots \quad (77)$$

In this case, all the terms of the array vanish with the

exception of the diagonal terms, so that it assumes the simple form

$$\begin{array}{ccc} D_{00} & 0 & 0 \\ 0 & D_{11} & 0 \\ 0 & 0 & D_{22}, \text{ etc.} \end{array}$$

If now we work out the differential coefficients (with respect to time) in such an array, we easily discover that all the terms of the new array must be equal to zero. For, according to equation (75) they are of the form

$$2\pi i v(n, m) D(n, m).$$

Those terms for which n differs from m must vanish, since D is a diagonal array, while those for which n equals m must also vanish, since, according to equation (74) $v(m, m)$ must equal zero.

What has been said already suggests the possibility of carrying out certain mathematical operations on a frequency array. We have already seen an example of such operations in the differentiation with respect to time. In a similar way we may define an array q'' as the sum or difference of two arrays q and q' , when

$$q''(n, m) = q(n, m) \pm q'(n, m) \dots \quad (78)$$

It is, however, more difficult to find a convenient definition of multiplication. Heisenberg defined q'' , the product of two arrays q and q' by the relation

$$q''(n, m) = \sum_k q(n, k) q'(k, m) \dots \quad (79)$$

i.e., the first term of the n th horizontal row of the first array is multiplied by the first term of the m th vertical column of the second array ; the second term of the n th horizontal row of the first array is then multiplied by the second term of the m th vertical column of the second array, and so on ; all these products are finally summed. It may readily be seen from this definition that multiplication is not commutative ; the result of the multiplication is different according to whether the first array is multiplied by the second, or *vice versa*. We may, accordingly,

speak of a multiplication difference of q and q' , represented by $q'q - qq'.$ *

Now Heisenberg founded his quantum mechanics on the assumption that the multiplication difference to be assigned to the momentum component of an electron in conjunction with the corresponding space co-ordinate is equal to the elementary quantum multiplied by a simple factor in the diagonal terms, while the remaining terms are zero. Thus, if, for the sake of brevity, we write

$$pq - qp = D \dots \dots \dots \quad (80)$$

where p represents the momentum components, then

$$D(n, m) = \begin{cases} zh & \text{for } m = n \\ 0 & \text{for } m \neq n \end{cases} \dots \dots \dots \quad (81)$$

where z is the factor mentioned above. That Heisenberg chose to take the product of momentum and space co-ordinate is quite comprehensible, since it is this product which, as physicists realised from the older quantum theory, has the dimensions of the quantity $h.$ †

It may easily be established by trial that the factor z in equation (81) must be given the value $1/2\pi i$ in order that the further conclusions may be in accordance with fact.

* For the sake of simplicity, let us assume that we have an array consisting of only two horizontal and two vertical rows, which we multiply by another similar array. We have thus to form the product

$$\begin{Bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{Bmatrix} \cdot \begin{Bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{Bmatrix}.$$

If we represent the product ab by c , and ba by d , we find from the multiplication rule (equation 79)

$$\begin{aligned} c_{11} &= a_{11}b_{11} = a_{12}b_{21} \\ c_{12} &= a_{11}b_{12} + a_{12}b_{22}, \end{aligned}$$

while

$$\begin{aligned} d_{11} &= a_{11}b_{11} + a_{21}b_{12} \\ d_{12} &= a_{12}b_{11} + a_{22}b_{12}. \end{aligned}$$

If the multiplication difference is f , then

$$\begin{aligned} f_{11} &= c_{11} - d_{11} = a_{12}b_{21} - a_{21}b_{12} \\ f_{12} &= c_{12} - d_{12} = a_{12}(b_{22} - b_{11}) + b_{12}(a_{11} - a_{22}), \text{ etc.} \end{aligned}$$

† Momentum has the dimensions gm.cm.sec^{-1} , and therefore the product of momentum and space co-ordinate has the dimensions $\text{gm.cm.}^2\text{sec}^{-1}$, or erg.sec.

Thus, if we represent by the symbol ϵ an array with a unit diagonal, of the following form

$$\begin{matrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{matrix} \text{etc.},$$

the so-called commutation rule of Heisenberg assumes the form

$$pq - qp = \frac{\hbar}{2\pi i} \epsilon \quad \dots \quad \dots \quad \dots \quad (82)$$

This equation shows that the error introduced by regarding momentum and space co-ordinate in the usual way as quantities interchangeable in multiplication is of the order of 10^{-27} . For macromechanics this error is naturally without significance. This is not, however, the case in atomic mechanics, where the right hand side of equation (82) (omitting the unitary factor, $i\epsilon$) is of the same order as the product of momentum and radius in the normal state of the hydrogen atom.

In the particular case where the quantity q has the usual significance of a Cartesian co-ordinate, the momentum term p is equal to the product of the mass, which will be represented by μ ,* and the corresponding velocity, so that we may also represent the momentum by a frequency array whose terms are equal to those of the velocity array (equation (75)) multiplied by the mass. The commutation rule then assumes the form

$$[\dot{q}q - q\dot{q}]_{nm} = \frac{\hbar}{2\pi i \mu} \epsilon_{nm} \quad \dots \quad \dots \quad \dots \quad (83)$$

Now, from equation (75)

$$[\dot{q}q]_{nm} = 2\pi i \sum_k \{ v(n, k) q(n, k) q(k, m) \}$$

and conversely

$$[q\dot{q}]_{nm} = 2\pi i \sum_k \{ q(n, k) v(k, m) q(k, m) \},$$

* Thus purposely avoiding the usual symbol m to obviate confusion with the index number m .

and therefore

$$[\dot{q}q - q\dot{q}]_{nm} = 2\pi i \sum_k \{ [\nu(n, k) - \nu(k, m)] q(n, k) q(k, m) \} \quad . \quad (84)$$

Thus, according to the commutation rule, when $m = n$, we have

$$\sum_k \{ [\nu(n, k) - \nu(k, n)] q(n, k) q(k, n) \} = -\frac{\hbar}{4\pi^2\mu} \quad . \quad (85)$$

In order to explain matters by a particularly simple example, we will return once more to the linear harmonic oscillator. The distance from the point of rest will be taken as the single co-ordinate. From earlier considerations (Chapter VII.) we know that in classical mechanics, to which we will adhere as closely as possible, the equation for the motion of the oscillator has the form

$$\frac{d^2q}{dt^2} + 4\pi^2\nu_0^2 q = 0 \quad . \quad . \quad . \quad . \quad (86)$$

where ν_0 is the frequency of the oscillator (the index 0 is added here, because it is necessary to distinguish between the fundamental frequency of the oscillator and the frequencies of the radiation emitted by it). In quantum mechanics, the corresponding frequency array given by equation (76) must be introduced in place of the co-ordinate or the acceleration. We therefore find

$$-4\pi^2\nu^2(n, m) q(n, m) + 4\pi^2\nu_0^2 q(n, m) = 0,$$

from which it follows that

$$\nu(n, m) = \pm \nu_0 \quad . \quad . \quad . \quad . \quad (87)$$

In the series of frequency terms made up with a constant index n and a variable m , only two terms, which must be neighbouring terms, can differ from zero, namely, those for which

$$m = \begin{cases} n - 1 \\ n + 1. \end{cases}$$

Similarly, in the series of frequency terms $\nu(n, m)$ formed

by keeping m constant and varying n , the only two differing from zero are those for which $n = (m - 1)$ or $(m + 1)$.

If, then, in the special case of the linear harmonic oscillator we build up a frequency array for the velocity or the momentum, only the following terms will differ from zero: in the first horizontal row the second term; in the second row the first and third terms; in the third row the second and fourth, and so on. A similar rule holds also for the vertical columns. If a term differing from zero is represented by an asterisk, an array for the velocity or the corresponding momentum is obtained in which the two oblique rows immediately adjoining and parallel to the principal diagonal consist of asterisks, thus:

$$\begin{array}{cccccc} 0 & * & 0 & 0 & 0 & 0 \\ * & 0 & * & 0 & 0 & 0 \\ 0 & * & 0 & * & 0 & 0 \\ 0 & 0 & * & 0 & * & 0 \\ 0 & 0 & 0 & * & 0 & * \text{ etc.} \end{array}$$

Returning to equation (85), we see that, in the sum which occurs in the equation, the only two terms differing from zero are those for which k is equal to n' or n'' , where the abbreviations n' and n'' are used for $(n + 1)$ and $(n - 1)$, respectively. Further, according to equation (73), $\nu(n, k)$ is equal but of opposite sign to $\nu(k, n)$, the numerical value of both, from equation (87), being ν_0 . Finally, it must be remembered that, if the index n' represents a state of more energy than that corresponding to n , radiation will be absorbed during the transition; thus the corresponding frequency must in this case be considered as negative; on the other hand, the state corresponding to n'' must then contain less energy, and an emission of radiation will occur during the transition; the corresponding frequency must then be taken as positive. The left hand side of equation (85) thus assumes the form

$$- 2\nu_0 [q(n, n') q(n', n) - q(n, n'') q(n'', n)].$$

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The commutation rule therefore leads to the relation

$$q(n, n') q(n', n) = q(n, n'') q(n'', n) + \frac{\hbar}{8\pi^2 \mu \nu_0}.$$

Since we begin the numbering of the rows with the index 0, we must assume all terms with negative indices to be zero. Using the following abbreviation

$$\frac{\hbar}{8\pi^2 \mu \nu_0} = Q \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (88)$$

we obtain the following relations

$$\begin{aligned} q(0,1) q(1,0) &= Q \\ q(1,2) q(2,1) &= q(0,1) q(1,0) + Q = 2Q \\ q(2,3) q(3,2) &= q(1,2) q(2,1) + Q = 3Q, \text{ etc.} \end{aligned}$$

In general, therefore,

$$q(n-1, n) q(n, n-1) = nQ \quad \dots \quad (89)$$

Now that we have obtained this equation as a particular expression of the commutation rule, we may try to use Heisenberg's method to calculate the energy values of the oscillator. From earlier considerations (Chapter VII), we have already seen that the potential energy of a linear harmonic oscillator is given by the expression

$$V = 2\pi^2 \nu_0^2 \mu q^2$$

(using the symbols μ for m , ν_0 for ν , and q for x). Adding to this the kinetic energy, $\frac{1}{2}\mu\dot{q}^2$, we obtain on the basis of classical mechanics the following expression for the total energy

$$E = 2\pi^2 \nu_0^2 \mu q^2 + \frac{\mu}{2} \dot{q}^2.$$

In quantum mechanics we replace the square of the coordinate, according to equation (79), by the relation

$$[q^2]_{nm} = \sum_k q(n, k) q(k, m) \quad \dots \quad (90)$$

Transforming the square of the velocity in a similar way, we obtain from equation (75) the relation

$$[\dot{q}^2]_{nm} = -4\pi^2 \sum_k \{v(n, k) v(k, m) q(n, k) q(k, m)\} \quad (91)$$

We may, therefore, obtain a frequency array for the energy also, as follows :

$$E(n, m) = 2\pi^2 \mu \sum_k \{[v_0^2 - v(n, k) v(k, m)] q(n, k) q(k, m)\} \quad (92)$$

If we first assume m and n in this equation to differ from one another, it follows from what has been said that all the summands disappear with the exception of those for which either n, k, m or m, k, n are three consecutive numbers. In such cases, however, $v(n, k)$ and $v(k, m)$ are both equal to v_0 , and of the same sign. The expression in square brackets in equation (92) is therefore zero. It thus follows that

$$E(n, m) = 0 \text{ for } m \neq n \dots \dots \quad (93)$$

The energy is therefore represented by a diagonal frequency array. This, as has already been said, in dealing with equation (77), signifies the invariability of the energy with time—in other words, the conservation of energy.

If, on the other hand, $m = n$, only those summands in equation (92) differ from zero for which $k = n'$ or n'' . For each of these two summands

$$v(n, k) v(k, n) = (+v_0) (-v_0).$$

We therefore obtain

$$E(n, n) = 4\pi^2 \mu v_0^2 [q(n, n') q(n', n) + q(n, n'') q(n'', n)].$$

On the basis of the commutation rule, as expressed by equation (89), we may write for this

$$E(n, n) = 4\pi^2 \mu v_0^2 [(n+1)Q + nQ].$$

The lowest value of the energy (E_0) is obtained by putting $n = 0$ in this equation ; we then obtain from equation (88)

$$E_0 = \frac{h\nu_0}{2}.$$

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For the higher energy values it follows from the last equation but one that

$$E_n = \frac{2n + 1}{2} h\nu_0 \dots \dots \quad (94)$$

The energy is therefore an odd multiple of a half energy element, and consequently it never disappears entirely. In this respect Heisenberg's quantum mechanics differs from the older quantum theory in exactly the same way as Schrödinger's theory. It also leads, on the basis of equation (87), to the important result that quantum changes are only possible between neighbouring states of the oscillator; finally, equation (94) also shows that, during such changes, the so-called frequency condition of Bohr is fulfilled, namely, that the frequency of the light quantum emitted or absorbed is equal to the energy change during the transition, divided by the elementary quantum of action.

CHAPTER IX

MATRIX MECHANICS

SOON after Heisenberg had developed his new ideas, Born and Jordan discovered a suitable mathematical apparatus for carrying out Heisenberg's programme. This was the method of matrices, a branch of mathematics to which little attention had hitherto been paid by physicists, which had, however, been thoroughly developed by the middle of the nineteenth century. By a matrix is generally meant a square array, whose terms are each characterised by two indices,* which follows the same rules, both for addition and multiplication (which is in general non-commutative), as those already developed by Heisenberg without the use of the matrix calculus. In the present chapter a general demonstration will be given by means of matrix mechanics that, as in the special case of the linear oscillator discussed in the previous chapter, the law of conservation of energy and Bohr's frequency condition follow as a necessary consequence of Heisenberg's commutation rule.

For the purposes of this proof, we must start from certain general facts of pure mathematics, in order to link up the argument with the considerations of the preceding chapter. Denoting matrices by thick type letters, let us first calculate the multiplication difference of two matrices, **D** and **A**, assuming the first to be a diagonal matrix. From equation (79) we find

$$[\mathbf{DA}]_{nm} = \sum_k \mathbf{D}(n, k) \mathbf{A}(k, m).$$

* In particular, a matrix is described as a Hermitean matrix when one term is transformed into the conjugate quantity (as in equation (72)), by interchanging the two indices.

By the definition of a diagonal matrix, only a single product in the summation differs from zero, namely, that for which $k = n$. Therefore

$$[\mathbf{D}\mathbf{A}]_{nm} = D(n, n) A(n, m),$$

while

$$[\mathbf{A}\mathbf{D}]_{nm} = \sum_k A(n, k) D(k, m).$$

In this summation also, only one product differs from zero, that for which $k = m$, and therefore

$$[\mathbf{A}\mathbf{D}]_{nm} = A(n, m) D(m, m).$$

We therefore obtain the following expression for the multiplication difference

$$[\mathbf{D}\mathbf{A} - \mathbf{A}\mathbf{D}]_{nm} = A(n, m) [D(n, n) - D(m, m)]. \quad (95)$$

From this equation it is at once seen that, in the special case where all the diagonal terms in the diagonal matrix are equal to one another, the multiplication difference vanishes, and the multiplication is therefore commutative.* Thus, if \mathbf{D} is a diagonal matrix in which $D(n, n) = D(m, m)$

$$\mathbf{D}\mathbf{A} - \mathbf{A}\mathbf{D} = 0 \quad \dots \quad (96)$$

The converse of this rule is naturally true also. If the multiplication of a matrix \mathbf{B} with any given matrix \mathbf{A} is found to be commutative, it may always be concluded that \mathbf{B} is a diagonal matrix, with equal terms. For the term n, m of the multiplication difference is given by

$$\sum_k \{B(n, k) A(k, m) - A(n, k) B(k, m)\},$$

and if, as assumed, \mathbf{A} is any matrix, the sum can only vanish in general when, firstly $B(n, m)$ vanishes for $m \neq n$, and secondly, $B(n, n) = B(m, m)$.

If a matrix ϵ , defined by the equation

$$\epsilon(n, m) = \begin{cases} 1 & \text{for } m = n \\ 0 & \text{for } m \neq n \end{cases} \quad \dots \quad (97)$$

* It may be seen from equation (95) that the commutative nature of the multiplication is general for any two diagonal matrices. For if \mathbf{A} and \mathbf{D} are both diagonal matrices, the term $A(n, m)$ on the right-hand side of equation (95) vanishes when $n \neq m$, while when $n = m$ the expression in square brackets is zero.

is called a unit matrix, it follows from equation (96) that the multiplication of any matrix with a unit matrix is commutative. The following relation is then always true

$$\epsilon \mathbf{A} = \mathbf{A} \epsilon \quad \dots \quad (98)$$

A matrix represented by the symbol \mathbf{A}^{-1} may now be regarded as the reciprocal of the matrix \mathbf{A} if

$$\mathbf{A} \mathbf{A}^{-1} = \epsilon \quad \dots \quad (99)$$

From this definition we see that a unit matrix is reciprocal to itself, for, by the laws of matrix multiplication

$$[\epsilon \epsilon]_{nm} = \sum_k \epsilon(n, k) \epsilon(k, m).$$

In this product, $\epsilon(n, k)$ vanishes whenever k is not equal to n , while $\epsilon(k, m)$ vanishes when m is not equal to k . We therefore find

$$(\epsilon \epsilon)_{nm} = \begin{cases} 1 & \text{for } m = n \\ 0 & \text{for } m \neq n. \end{cases}$$

Therefore, according to equation (97)

$$\epsilon \epsilon = \epsilon,$$

or, from equation (99)

$$\epsilon^{-1} = \epsilon \quad \dots \quad (100)$$

Thus, by regarding division by a matrix as multiplication by its reciprocal matrix, we may define the differential coefficient of a matrix function

$$\mathbf{y} = \mathbf{f}(\mathbf{x}),$$

with respect to an argument matrix (\mathbf{x}) by the relation,

$$\frac{d\mathbf{y}}{d\mathbf{x}} = \lim_{\mathbf{a} = 0} \frac{\mathbf{f}(\mathbf{x} + \mathbf{a}) - \mathbf{f}(\mathbf{x})}{\mathbf{a}} \quad \dots \quad (101)$$

where the matrix \mathbf{a} is formed by multiplication of the unit matrix by a pure number, thus

$$\mathbf{a} = a \epsilon.$$

Then, according to equation (100)

$$\frac{d\mathbf{y}}{d\mathbf{x}} = \lim_{a=0} \frac{1}{a} \{ [\mathbf{f}(\mathbf{x} + a \epsilon) - \mathbf{f}(\mathbf{x})] \epsilon \}. \quad \dots \quad (102)$$

In the particular case where $\mathbf{y} = \mathbf{x}$, we obtain, by taking into account the rules for matrix multiplication

$$\begin{aligned} \left[\frac{d\mathbf{x}}{d\mathbf{x}} \right]_{nm} &= \lim_{\alpha \rightarrow 0} \frac{1}{\alpha} \sum_l \{ [x(n, l) + \alpha \epsilon(n, l) - x(n, l)] \epsilon(l, m) \} \\ &= \sum_l \epsilon(n, l) \epsilon(l, m) = (\epsilon \epsilon)_{nm}. \end{aligned}$$

Therefore

$$\frac{d\mathbf{x}}{d\mathbf{x}} = \epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (103)$$

Now, let $\mathbf{f}(\mathbf{x})$ and $\mathbf{g}(\mathbf{x})$ be any two functions of the argument matrix \mathbf{x} . If we form the product of the two matrices $\mathbf{f}\mathbf{g}$ and differentiate this with respect to \mathbf{x} , we find, according to equation (101)

$$\frac{d(\mathbf{f}\mathbf{g})}{d\mathbf{x}} = \lim_{\mathbf{a} \rightarrow 0} \frac{1}{\mathbf{a}} [\mathbf{f}(\mathbf{x} + \mathbf{a})\mathbf{g}(\mathbf{x} + \mathbf{a}) - \mathbf{f}(\mathbf{x})\mathbf{g}(\mathbf{x})],$$

or, by adding and subtracting the term $\mathbf{f}(\mathbf{x} + \mathbf{a})\mathbf{g}(\mathbf{x})$ in the square brackets :

$$\begin{aligned} \frac{d(\mathbf{f}\mathbf{g})}{d\mathbf{x}} &= \lim_{\mathbf{a} \rightarrow 0} \frac{1}{\mathbf{a}} \{ \mathbf{f}(\mathbf{x} + \mathbf{a})\mathbf{g}(\mathbf{x} + \mathbf{a}) - \mathbf{f}(\mathbf{x} + \mathbf{a})\mathbf{g}(\mathbf{x}) \\ &\quad + \mathbf{f}(\mathbf{x} + \mathbf{a})\mathbf{g}(\mathbf{x}) - \mathbf{f}(\mathbf{x})\mathbf{g}(\mathbf{x}) \}. \end{aligned}$$

Therefore, from equation (101)

$$\frac{d(\mathbf{f}\mathbf{g})}{d\mathbf{x}} = \mathbf{f} \frac{d\mathbf{g}}{d\mathbf{x}} + \frac{d\mathbf{f}}{d\mathbf{x}} \mathbf{g} \quad . \quad . \quad . \quad . \quad . \quad (104)$$

If we put, for instance,

$$\mathbf{f}(\mathbf{x}) = \mathbf{g}(\mathbf{x}) = \mathbf{x}$$

then, according to equations (103) and (104)

$$\frac{d(\mathbf{x}^2)}{d\mathbf{x}} = 2\mathbf{x}\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (105)$$

Let us now consider the case of a matrix \mathbf{W} , which is a function of the two argument matrices \mathbf{p} and \mathbf{q} , whose multiplication difference is a matrix $k\epsilon$, so that

$$\mathbf{pq} - \mathbf{qp} = k\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (106)$$

It may then readily be shown that the following two equations are fulfilled

$$\left. \begin{aligned} \mathbf{Wq} - \mathbf{qW} &= k \frac{\partial \mathbf{W}}{\partial \mathbf{p}} \\ \mathbf{pW} - \mathbf{Wp} &= k \frac{\partial \mathbf{W}}{\partial \mathbf{q}} \end{aligned} \right\} \quad \dots \quad (107)$$

The proof may be obtained in the following way. It is first assumed that the equations (107) may be true for any two functions \mathbf{f} and \mathbf{g} . Taking, first $\mathbf{W} = \mathbf{f}$, and then $\mathbf{W} = \mathbf{g}$, it is seen at once that the equations (107) are also true when $\mathbf{W} = \mathbf{f} + \mathbf{g}$. Further, however, it may be shown in that case that the equations must also be true when $\mathbf{W} = \mathbf{f.g}$. This is seen by making use of the identity

$$\mathbf{fgq} - \mathbf{qfg} = \mathbf{f}(\mathbf{gq} - \mathbf{qg}) + (\mathbf{fq} - \mathbf{qf})\mathbf{g}$$

(i.e., the term \mathbf{fqg} is added and subtracted again). Now, since it has been postulated that equations (107) are true for \mathbf{f} and \mathbf{g} , the first expression in brackets in the last equation is equal to $k \frac{\partial \mathbf{g}}{\partial \mathbf{p}}$, and the expression in the second bracket is equal to $k \frac{\partial \mathbf{f}}{\partial \mathbf{p}}$. We therefore obtain

$$\mathbf{fgp} - \mathbf{qfg} = k \left(\mathbf{f} \frac{\partial \mathbf{g}}{\partial \mathbf{p}} + \frac{\partial \mathbf{f}}{\partial \mathbf{p}} \mathbf{g} \right)$$

or, from equation (104) :

$$(\mathbf{fg})\mathbf{q} - \mathbf{q}(\mathbf{fg}) = k \frac{\partial(\mathbf{fg})}{\partial \mathbf{p}}.$$

Similarly,

$$\mathbf{p}(\mathbf{fg}) - (\mathbf{fg})\mathbf{p} = k \frac{\partial(\mathbf{fg})}{\partial \mathbf{q}}.$$

If, therefore, equations (107) are true for any two functions, \mathbf{f} and \mathbf{g} , they also hold for the functions $\mathbf{f} + \mathbf{g}$ and $\mathbf{f.g}$. Thus, as long as they are true for \mathbf{f} and \mathbf{g} they must also be fulfilled in the case of any function which can be

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formed by repeated additions and multiplications from **f** and **g**. But the equations are true, as can readily be seen, both for **W** = **p** and for **W** = **q**; therefore, they must be true for any whole function of **p** and **q**, which proves our proposition.

After this general mathematical discussion, we may return to physics, and regard **q** as a co-ordinate matrix and **p** as the corresponding momentum matrix. We first take the equations of motion of classical mechanics, writing them for the sake of convenience in the so-called canonical form, in which the energy is regarded as a function of the co-ordinates and the momenta (as a Hamiltonian function **H** (*q*, *p*)). For the values of this Hamiltonian function a matrix may also be formed, and the canonical equations of motion may then be written,

$$\left. \begin{aligned} \dot{\mathbf{q}} &= \frac{\partial \mathbf{H}}{\partial \mathbf{p}} \\ \dot{\mathbf{p}} &= -\frac{\partial \mathbf{H}}{\partial \mathbf{q}} \end{aligned} \right\} \dots \dots \dots \quad (108)$$

where **H**, **q** and **p** are written in thick type to represent the transference to matrix mechanics.

The Hamiltonian function **H** representing the energy, must satisfy equations (107), since it is a function of **q** and **p**. Therefore, giving the constant *k* the value $h/2\pi i$ in accordance with Heisenberg's commutation rule, we obtain the two relations

$$\left. \begin{aligned} \mathbf{Hq} - \mathbf{qH} &= \frac{h}{2\pi i} \dot{\mathbf{q}} \\ \mathbf{pH} - \mathbf{Hp} &= -\frac{h}{2\pi i} \dot{\mathbf{p}} \end{aligned} \right\} \dots \dots \dots \quad (109)$$

In the following discussion we may confine ourselves to the first of these two equations.

This equation may now be easily related to the spectral terms whose differences represent the spectral frequencies

produced by any electron under consideration. For this purpose we arrange the terms in a diagonal matrix, thus :

$$\begin{matrix} T_{00} & 0 & 0 \\ 0 & T_{11} & 0 \\ 0 & 0 & T_{22} \end{matrix} \text{ etc.,}$$

where, from the definition of the spectral terms,*

$$T(n, n) - T(m, m) = v(n, m) \dots \quad (110)$$

By multiplying the diagonal matrix of the terms by the co-ordinate matrix, we obtain, according to equation (95),

$$[T\mathbf{q} - \mathbf{q}T]_{nm} = q(n, m) [T(n, n) - T(m, m)],$$

or, from equation (110),

$$[T\mathbf{q} - \mathbf{q}T]_{nm} = q(n, m)v(n, m).$$

According to equation (75) the following relation is therefore obtained,

$$T\mathbf{q} - \mathbf{q}T = \frac{1}{2\pi i} \mathbf{q} \dots \dots \quad (111)$$

and, by comparison with equation (109),

$$\mathbf{H}\mathbf{q} - \mathbf{q}\mathbf{H} = h(T\mathbf{q} - \mathbf{q}T)$$

or

$$(\mathbf{H} - hT)\mathbf{q} - \mathbf{q}(\mathbf{H} - hT) = 0 \dots \quad (112)$$

According to what was said about equation (96), this means that the matrix $(\mathbf{H} - hT)$ is a diagonal matrix with equal diagonal terms. But \mathbf{T} itself is a diagonal matrix, and we therefore see that the energy matrix must also be a diagonal matrix whose terms must differ from those of the diagonal matrix hT only by an

* The knowledge that the duplex manifold of the spectral frequencies of an atom could be related to a simple manifold of term values is older than the quantum theory of the atom; it was discovered by Ritz (1908) before the frequency condition of Bohr had been propounded. Ritz's ideas were directly connected with previous work of Rydberg. In any case the so-called Rydberg-Ritz term principle was developed quite independently of the quantum theory.

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additive constant, which is equal for all the members. It follows that

$$H(n, m) = 0 \text{ for } n \neq m \dots \dots \dots \quad (113)$$

and, further, that

$$H(n, n) - H(m, m) = \hbar[T(n, n) - T(m, m)] \dots \dots \dots \quad (114)$$

From the fact that \mathbf{H} is a diagonal matrix, it follows from what was said after equation (77) that

$$\mathbf{H} = 0 \dots \dots \dots \dots \dots \dots \quad (115)$$

This matrix equation expresses the law of the conservation of energy. Further, from equations (110) and (114), the following relation is obtained :

$$H(n, n) - H(m, m) = \hbar\nu(n, m) \dots \dots \dots \quad (116)$$

This equation again is the expression of the Bohr frequency condition, relating an atomic change of state to a light quantum whose frequency is determined by the quotient of the energy change and the elementary quantum of action. In quantum mechanics, therefore, the conservation of energy and the frequency condition are actually seen to follow as necessary consequences of the Heisenberg commutation rule.

In the original theory of Bohr, the elementary quantum of action appeared in a double capacity, both as an optical and a mechanical constant. The first *rôle* was expressed in the Bohr frequency condition, the second in Bohr's rule of quantisation, which equates 2π times the angular momentum with an integral multiple of the elementary quantum. How one and the same quantity could play two such different *rôles*, the undulatory and the dynamic, was quite unintelligible from Bohr's theory. The theory of de Broglie regarded the undulatory *rôle* of the quantum as its primary function, and thence was able to deduce the dynamic *rôle* as a necessary consequence. Quantum mechanics attempts the converse proposition, regarding the dynamic as the primary *rôle*, and from this deducing the undulatory and spectroscopic significance of the elementary quantum of action.

CHAPTER X

THE RELATION BETWEEN HEISENBERG'S QUANTUM MECHANICS AND THE THEORY OF SCHRÖDINGER

THE fact that Schrödinger brought out his mechanics of characteristic values a few months after the appearance of Heisenberg's work on quantum mechanics obviously raised the question of a possible connection between the two theories. Schrödinger himself * was able to discover this connection, and to prove that, in spite of the diversity of view point his theory was, nevertheless, completely equivalent mathematically to the quantum mechanics of Heisenberg and Born. The rigid proof of this equivalence is, however, too involved, and requires too much previous mathematical knowledge to permit of its introduction within the limits of a treatise whose elementary character has to be maintained. It is only possible in the following pages to enter upon some of the fundamental ideas of the proof.

For this purpose, the starting point is the conception of the mathematical operator. The differentiation of a function y with respect to an argument, x , may be regarded symbolically as the multiplication of y by the operator \dagger d/dx . In a similar manner the second partial differential coefficient of y with respect to x may be regarded as multiplication of y by an operator, $\partial^2/\partial x^2$. Further, x itself may be regarded as an operator, so that the operator x

* E. Schrödinger, "Über das Verhältnis der Heisenberg-Born-Jordanschen Quantenmechanik zu der meinen," *Ann. d. Phys.* (4), **79**, (1926), p. 734.

† The so-called Hamiltonian operator ∇ is generally known in vector analysis. This operator may be regarded as a vector with the components $\partial/\partial x$, $\partial/\partial y$, $\partial/\partial z$, and may be used in calculations in the same way as a vector.

means multiplication by x ; thus, we may speak of an operator 1 , which, when applied to any function, gives the same function once more. By the product of two operators is understood an operator which leads to the same result as the successive application of the operators separately. The second differential coefficient is then seen to be the square of the first, and the operator product $\frac{d}{dx}x$, signifies differentiation with respect to x of the product of x and a function.

On the foregoing grounds the multiplication of two operators is seen to be non-commutative; commutation relations can, therefore, also be developed for operators. For this purpose the following identity may be used :

$$\frac{\partial(xy)}{\partial x} = y + x \frac{\partial y}{\partial x}.$$

By confining ourselves to the operators in this equation and omitting the function y , we may write the operator equation :

$$\frac{\partial}{\partial x}x - x \frac{\partial}{\partial x} = 1 \quad \dots \dots \dots \quad (117)$$

this means to say that if we multiply any function by x , differentiate the product thus obtained with respect to x and subtract from the result x times the differential coefficient (with respect to x) of the function itself, we arrive at the original function once more.

Equation (117) may, of course, be multiplied by any constant.* If we choose as the constant the expression $h/(2\pi i)$, and replace the operator x , signifying multiplication by x , by the operator q , i.e., multiplication by the co-ordinate q , we obtain a commutation relation of the form,

$$\frac{h}{2\pi i} \frac{\partial}{\partial q} q - q \frac{h}{2\pi i} \frac{\partial}{\partial q} = \frac{h}{2\pi i} 1 \quad \dots \dots \dots \quad (118)$$

Comparison of this relation with the commutation rule of Heisenberg (equation (82)) shows that, if the co-ordinate

* Since $d(ay)/dx$ is equal to $a dy/dx$ when a is a constant.

matrix is replaced by the operator q (multiplication by q), the momentum matrix must be replaced by the operator :

$$\frac{\hbar}{2\pi i} \frac{\partial}{\partial q} \dots \dots \dots \dots \dots \dots \quad (119)$$

This important result, noticed first by Born and Wiener,* suggests that a generalisation of mechanics might be obtained from one of the fundamental equations of classical mechanics, connecting the co-ordinate q and the momentum p , by replacing q by the operator q and p by the operator of expression (119). For the purpose we may conveniently choose the energy principle. If we consider a single particle, denoting its co-ordinates by q_x , q_y , and q_z , we have for the kinetic energy

$$L = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2),$$

where $p_x = m\dot{q}_x$, etc. Denoting the potential energy, which depends only on the co-ordinates, by V , and the total energy by E , we may express the law of conservation of energy by the following equation :

$$\frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V - E = 0 \dots \dots \quad (120)$$

If, now, we regard the left-hand side of this equation as an operator, we must, according to expression (119), replace the expression in brackets in equation (120) by

$$\left(\frac{\hbar}{2\pi i} \right)^2 \left(\frac{\partial^2}{\partial q_x^2} + \frac{\partial^2}{\partial q_y^2} + \frac{\partial^2}{\partial q_z^2} \right) = - \frac{\hbar^2}{4\pi^2} \Delta,$$

where Δ is the Laplace operator (cf. equation (47)). If, then, S is any function of the co-ordinates, we obtain the relation

$$\left\{ - \frac{\hbar^2}{8\pi^2 m} \Delta + V - E \right\} S = 0 \dots \dots \quad (121)$$

* M. Born and Norbert Wiener, *Zeitschr. f. Phys.* **36**, (1926), p. 174.

or

$$\Delta S + \frac{8\pi^2 m}{h^2} (E - V) S = 0.$$

In this equation we recognise once more the fundamental equation of Schrödinger's theory (equation (52)). It is thus an extension of classical mechanics by the application of Heisenberg's commutation rule to operators.

If we consider a system of particles instead of an isolated particle, representing the momentum components of the n th particle by p_{nx} , p_{ny} , p_{nz} , equation (120) assumes the form :

$$\sum_n \frac{1}{2m_n} (p_{nx}^2 + p_{ny}^2 + p_{nz}^2) + V - E = 0,$$

where V and E represent the potential and total energy of the system respectively. Equation (121) must then be written in the form

$$\left\{ -\frac{h^2}{8\pi^2} \sum_n \frac{1}{m_n} \Delta_n + V - E \right\} S = 0 \quad \dots \quad (122)$$

and from this we obtain the generalised form of Schrödinger's differential equation (cf. equation (65)) as follows :

$$\sum_n \frac{1}{m_n} \left(\frac{\partial^2 S}{\partial x_n^2} + \frac{\partial^2 S}{\partial y_n^2} + \frac{\partial^2 S}{\partial z_n^2} \right) + \frac{8\pi^2}{h^2} (E - V) S = 0.$$

From the solutions given by Schrödinger's differential equation in any special case, the matrix elements belonging to the corresponding quantum mechanical problem may now be actually calculated. If we denote the characteristic values of Schrödinger's problem by A_0 , A_1 , A_2 , etc., arranging and numbering them in order of magnitude, and the corresponding solutions (*i.e.*, the characteristic functions) by ϕ_0 , ϕ_1 , ϕ_2 , etc., we may build up a two-dimensional manifold of values according to the formula :

$$a(n, m) = \int_{-\infty}^{+\infty} \phi_n(q) q \phi_m^*(q) dq \quad \dots \quad (123)$$

and a second two-dimensional manifold according to the second formula :

$$b(n, m) = \frac{\hbar}{2\pi i} \int_{-\infty}^{+\infty} \phi_n(q) \frac{\partial \phi_m^*(q)}{\partial q} dq \quad \dots \quad (124)$$

In these equations ϕ^* is the complex quantity conjugate to ϕ . Schrödinger and Eckart [†] have shown that equations (123) and (124) actually represent the solution of the problem from the standpoint of quantum mechanics, since

$$q(n, m) = a(n, m) e^{2\pi i v(n, m)t} \quad \dots \quad (125)$$

and

$$p(n, m) = b(n, m) e^{2\pi i v(n, m)t} \quad \dots \quad (126)$$

The complicated proof must, however, be omitted here.

The problems of atomic physics can thus be solved by Schrödinger's method of characteristic values. The application of this method is essentially simpler than the direct use of the matrix theory, and by means of a transformation on the basis of equations (123) and (124) is capable of yielding the solution to the problem of matrix mechanics also. This solution gives, in the form of the quantities $a(n, m)$ the probabilities of transition which determine the intensity of the spectral lines.

In addition to its relationship to Schrödinger's theory of characteristic values, matrix mechanics has several points of contact with a third theory of atomic mechanics which was also developed in 1925 ; this is the mechanics of q -numbers founded by Dirac.[‡] The theory employs the assumption that the magnitudes of quantum mechanics may be represented by a kind of "super-complex" number, called by Dirac a q -number, and distinguished by him from ordinary numbers (called by Dirac c -numbers) by the fact that multiplication is non-commutative. Dirac's theory employs q -numbers to represent not only the co-ordinates and momenta, together with the energy (as a function of co-ordinate and

[†] C. Eckart, *Phys. Rev.* **28**, (1926), p. 711.

[‡] P. A. M. Dirac, *Proc. Roy. Soc., London, A.*, **109**, (1926), p. 642; **110**, (1926), p. 561.

momentum) but also the time.* The results obtained by the application of Dirac's theory to special problems of atomic physics are in agreement with the conclusions drawn from Schrödinger's and Heisenberg's theories.

* In Dirac's theory the time and the spatial co-ordinates are of the same nature, namely, *q*-numbers. The transformation to relativity theory is therefore much easier than with matrix mechanics, where the spatial co-ordinates appear as matrices while the time is an ordinary quantity.

CHAPTER XI

THE CAUSAL AND THE STATISTICAL VIEWS IN ATOMIC PHYSICS

THE complete mathematical equivalence which connects the theories of Schrödinger and Heisenberg-Born-Jordan, in spite of their antagonistic aims, renders particularly important the question of how the central idea of each theory is to be interpreted in the light of the other. In the central position in Schrödinger's theory stands the conception of the wave, in the centre of quantum mechanics the idea of the corpuscle. What is the meaning of the electron from Schrödinger's point of view, and of a material wave from Heisenberg's standpoint ?

The first question has already been answered by de Broglie himself, who regarded the material particles as positions of maximum energy density within the wave. Schrödinger has carried this idea still further for the special case of a linear oscillator. If ψ_n ($n = 0, 1, 2, 3$, etc.) are the solutions of the fundamental equation of wave mechanics for this special case, Schrödinger * considered a group of characteristic functions (*i.e.*, of characteristic vibrations) for which all the values of n lie in the immediate neighbourhood of some large number ; the frequencies are then limited to a narrow region. Schrödinger was then able to show that by the superposition of the characteristic vibrations of this narrow region a relatively high and narrow "hump" is obtained, which moves backwards and forwards in the same way as a linear oscillating particle. He further showed that such

* F. Schrödinger, "Der stetige Übergang von der Mikro-zur Makromechanik, Naturwissenschaft, 14, (1926), p. 664 (also in "Abhandlungen zur Wellenmechanik").

a group of waves, such an "energy packet," can under certain circumstances be held together so long (*i.e.*, concentrated into a restricted but constantly advancing region) that in a given time the generally inevitable dissolution of the energy packet does not occur to a noticeable extent.*

An interpretation of material waves on the basis of quantum mechanics, the converse of Schrödinger's explanation, was first given by Born.† Schrödinger's theory is concerned with the establishment of a strict causal relationship. It is founded, in the first place, on the assumption that the state of the wave field may be exactly described at any instant, and in the second place on the postulate that the state of the field at any time must be deducible from its original state at some earlier time. In addition, the fundamental differential equation of Schrödinger's theory is of the type which is peculiar to classical causal physics. It seems puzzling at first that such an equation, postulating, as it does, causality, continuity, and space-time arrangement, can nevertheless (as is seen from the mathematical equivalence between Schrödinger's and Heisenberg's theories) give correct results when applied in the region of quantum mechanics, which is essentially discontinuous, and cannot be given a space-time representation in the ordinary sense.

The explanation of this apparent contradiction was found by Born, who interpreted the Schrödinger field scalar, which is propagated in wave form in the configuration-space in accordance with Schrödinger's differential

* If ω_0 is the original breadth of the wave bundle and m its mass, its breadth in the absence of outside forces is given, at time t , by the formula (Ehrenfest, *Zeitschr. f. Phys.* **45**, (1927), p. 455)

$$\omega^2 = \omega_0^2 + \frac{\hbar^2}{4\pi^2 m^2 \omega_0^2} t^2.$$

The time necessary for doubling of the original breadth, for example, in the case of a mass of 1 gm. and an original breadth of 10^{-3} cm., amounts to no less than 10^{13} years approximately. For the mass of a proton and an original breadth of 10^{-8} cm., on the other hand, the corresponding time is only 10^{-18} sec.

† M. Born, *Zeitschr. f. Physik* **37**, (1926), p. 863; **38**, (1926), p. 803.

equation, as a probability in the statistical sense. Such an interpretation is supported by the connection between the light quantum hypothesis and the classical undulatory theory. In this theory the light intensity at a given spot is given as the square of the amplitude at that spot, while on the basis of the light quantum hypothesis it can only be connected with the probability of the arrival of a light quantum at the spot in question.* Such an interpretation reconciles the idea that the direction of motion of an individual light quantum is indeterminate with the strict regularity shown by observable optical phenomena such as interference and diffraction.

The far-reaching analogy between light quanta and electrons † suggests the possibility of expressing the latter in terms of Schrödinger waves. In the configuration-space corresponding to n particles (this is $3n$ -dimensional, so that, for example, for two particles it would be six-dimensional), the configuration of the system at any instant may be represented by the position of a characteristic point. From the standpoint of Born, it is impossible at any instant to say where this point will be at the next instant, *i.e.*, what will be its direction of motion in the configuration-space. All that quantum mechanics can do, according to Born, is to give the probability of its travelling in a given direction. This probability can, however, be treated as a continuously variable determinate quantity, which can, therefore, satisfy a differential equation of the "classical" type such as Schrödinger's.‡

The fact that a causal conception of atomic physics encounters fundamental difficulties was pointed out by

* This interpretation renders superfluous the inexplicable assumption of mutual destruction of light quanta; for it shows that under certain circumstances the probability of the arrival of light quanta at a given spot, in spite of its proximity to the light source, may be so small that the spot remains dark.

† This analogy is brought out particularly clearly in a publication by G. Beck, *Zeitschr. f. Phys.* **43**, (1927), p. 658.

‡ Schrödinger himself tried to relate the field scalar in his equation with the density of electrical charge. See E. Schrödinger, "Quantisierung als Eigenwertproblem," 4th paper, § 7.

Heisenberg,* who showed that even in an imaginary experiment it would be impossible to combine in a single measurement an ideally accurate determination of a coordinate with an ideally accurate determination of the corresponding momentum, and that therefore of necessity every measurement of atomic magnitudes must be attended with uncertainty.

If we consider, for example, an electron revolving within an atom, we might perhaps be able to determine by means of a single measurement its position and its momentum (*i.e.*, its velocity). For the purpose we should have to "illuminate" the electron under a "microscope" and then to determine its velocity by means of the Doppler effect, *i.e.*, by the alteration of wavelength suffered by the illuminating rays during reflection by the moving electron. With this observation, however, there would of necessity be associated a Compton effect, inasmuch as the velocity of the electron would be changed by the impact of a light quantum upon it.

Now the shorter the wavelength of the illuminating rays, the greater would be the possible accuracy of the determination of the position of the electron ; it would at least be necessary to use γ -rays, whose wavelength is from five to fifty times smaller than the radius of the normal hydrogen atom † on the Bohr theory. On the other hand, the shorter the wavelength, the greater will be the Compton effect, and consequently the greater will be the change in the momentum of the electron during and after the observation. If, therefore, the greatest accuracy is required in the determination of the velocity by means of the Doppler effect, the longest possible wavelength must be chosen in order that the error due to the unavoidable Compton effect may be as small as possible. If, however, the waves are long, then, according to what has been said

* W. Heisenberg, "Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik," *Zeitschr. f. Phys.* **43**, (1927), p. 172.

† The wavelength of hard γ -rays is between 10^{-10} and 10^{-9} cm., the normal radius of the hydrogen atom about 5.10^{-9} cm.

above, an accurate determination of the position of the electron will be impossible. Accuracy in determination of the position is thus only possible at the sacrifice of accuracy in the measurement of the momentum, and *vice versa*. The commutation rule (equation (82)) must, according to Heisenberg, be the exact expression of the uncertainty; in general, in the case of the greatest possible precision, the product of the errors involved in the measurement of co-ordinate and momentum is, according to Heisenberg, determined by the elementary quantum of action, and must be equal in order of magnitude to it.

Since now a precise description of atomic processes in the classical sense is impossible, the causal principle also naturally loses its significance for physics. For this principle, according to which the exact knowledge of the present renders possible an exact calculation of the future, is meaningless when an exact knowledge of the present is unattainable. Causality must, therefore, according to the theories of quantum mechanics, be discarded in dealing with the elementary processes of physics, and can only be accepted in the case of the probabilities to be ascribed on statistical grounds to these individual processes.

CHAPTER XII

PAULI'S PRINCIPLE AND THE QUANTUM THEORY OF THE PERIODIC TABLE

THE results of quantum mechanics stand in close relationship to certain important conclusions, which were drawn by Pauli a year before the development of Heisenberg's theory, with regard to the periodic system of the elements. It may well be said that the development of the problem of the elements offers one of the most striking examples of how all scientific advance finally consists in the gradual replacement of qualitative by quantitative knowledge. In the case of this problem the quantitative development was made possible, first by the discovery of the electrons, which enabled the qualitative differences of the chemical elements to be referred to differences in the arrangement of the ultimate particles, and secondly by the discovery by Moseley in 1913, of the natural series of the elements. In the natural series, each element has a definite atomic number corresponding with its position in the series (e.g., hydrogen has the atomic number 1, helium 2, iron 26, gold 79, and uranium the highest number, 92); and this number is the same as the number of electrons surrounding the nucleus in the neutral state of the atom.

By the discovery of the atomic numbers of the elements an exact representation of chemical periodicity was made possible. The recognition of seven periods in the system of the elements dates back to the year 1870 *; but only after Moseley's discovery was it possible to determine

* The periodic system of the elements was discovered simultaneously by Lothar Meyer and Mendeleeff.

exactly the lengths of the periods * as containing 2, 8, 8, 18, 18 and 32 members respectively. The fundamental problem of the modern theory of the elements was to obtain an explanation of these numbers on a quantum basis. The numbers are the more interesting to physicists since they are each equal to twice a perfect square.† An important step towards the solution of the problem was achieved, in 1924, by Pauli, by the application of the principle of the four-fold quantisation of the atomic states.

To aid in the understanding of this principle on the basis of quantum mechanics, a discussion of matrix theory may first be interpolated, dealing with the angular momentum of a system of particles symmetrical about an axis. On account of the tediousness of the necessary calculations, only the results will be given here, following Born, whose original work ‡ should be consulted for details. The angular momentum about the axis for such a system is equal to the resultant of the angular momenta of the individual particles composing the system, and the angular momentum of each is given by the product of its mass, velocity and distance from the axis.

From the commutation rule of matrix mechanics it may be deduced on the lines of classical mechanics that the matrix corresponding to the angular momentum about the axis (U) is a diagonal matrix, and also that its terms (U_0 , U_1 , U_2 , etc.) stand in a simple relation to the co-ordinate matrices (of which there must be three for each particle, corresponding to the three spatial co-ordinates). Thus, if we make the z -axis the axis of symmetry, and denote the co-ordinate matrices of a given particle by \mathbf{q}_x , \mathbf{q}_y , \mathbf{q}_z , we obtain the following three equations for each

* The seventh period ceases at the sixth member with uranium. All the periods begin with an alkali metal (except in the case of the first period, which starts with hydrogen) and end with an inactive gas.

† $2 = 2.1^2$; $8 = 2.2^2$; $18 = 2.3^2$; $32 = 2.4^2$.

‡ Max Born, "Problems of Atomic Dynamics" (Cambridge, U.S.A., 1926), Part I., Lecture 16.

particle, connecting the individual co-ordinates with the total angular momentum :

$$\left. \begin{aligned} q_x(n, m) (U_n - U_m) &= \frac{h}{2\pi i} q_y(n, m) \\ q_y(n, m) (U_n - U_m) &= -\frac{h}{2\pi i} q_x(n, m) \\ q_z(n, m) (U_n - U_m) &= 0. \end{aligned} \right\} \dots \dots \quad (127)$$

We can now distinguish two different kinds of change of state—of so-called “ quantum jumps ”—in the system, according to whether the angular momentum about the axis alters during the change or not. Considering the first case (more detailed discussion must be postponed to a later chapter), and multiplying together the first two equations (127), we obtain

$$U_n - U_m = \pm \frac{h}{2\pi} \dots \dots \quad (128)$$

In general, therefore, we may write

$$U_n = U_o + n' \frac{h}{2\pi},$$

where n' is an integer, either positive or negative, and U_o is a constant.

Calculations on the basis of the matrix calculus lead, however, to the conclusion that the sum of the values of U for all possible values of n' must vanish. This means that

$$\sum_{n'} (n' + n_o) = 0 \dots \dots \quad (129)$$

if we write

$$U_o = n_o \frac{h}{2\pi}.$$

Since two adjacent values in this series differ by unity (for according to equation (128) n' must either change by unity or remain unaltered) and since further (from equation (129)) the series of values of $(n' + n_o)$ must be sym-

metrically grouped about zero, there are only two possibilities. The series is either

$$\dots -3, -2, -1, 0, +1, +2, +3 \dots$$

or

$$\dots -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}, +\frac{5}{2} \dots$$

The quantity $(n' + n_o)$, which will in future be designated* m , has the significance of a quantum number. It is the "magnetic quantum number" already used in the older quantum theory to explain the Zeeman effect. As may be seen from the preceding remarks (equation (128)) the magnetic quantum number must either remain unaltered during a change of atomic state, or change by ± 1 .

Considerations of matrix mechanics lead to a further quantum number when, instead of the angular momentum (U) about the axis of symmetry, we take the total angular momentum (M), which differs from (U) when external forces are present. It may be shown that for the limiting case of infinitely small external forces the total angular momentum may be arranged as a diagonal matrix whose terms are equal to M_j^2 , where

$$M_j = \frac{\hbar}{2\pi} \sqrt{j(j+1)} \dots \dots \dots \quad (130)$$

In this formula, which corresponds with one of the results of Schrödinger's theory (equation (61)), j again represents a quantum number which, as further consideration will show, resembles the magnetic quantum number in remaining unaltered or changing by unity during quantum changes. A close connection exists between the m and j quantum numbers, since, in the state represented by the j quantum number, the magnetic quantum number m may assume all values between $-j$ and $+j$ differing from each other by unity, but only those values. The two quantum numbers, m and j , are therefore additional to

* This symbol has of course nothing to do with the letter m used previously as a suffix.

the principal quantum number, which characterises the energy of that electron which produces the spectral line during its transition. The quantum number here designated by j was already known in the older theory. It was introduced into atomic physics, in 1920, by Sommerfeld as the inner quantum number.

In order to arrive finally at a four-fold quantisation of atomic states, it is necessary to introduce the hypothesis founded in 1925 by Uhlenbeck and Goudsmit,* that the individual electrons perform a spinning motion which confers upon them the property of small magnets. Each electron thus possesses an angular momentum in virtue of this motion ; in this connection it must be remembered that there are two opposite possibilities for this rotation. Heisenberg and Jordan have shown † that the application of quantum mechanics to spectroscopic observations leads to the result that the angular momentum ascribed to a spinning electron must be such that the difference in the two opposite directions of spin corresponds to the quantum number 1. The angular momentum of each electron

must, therefore, correspond to a quantum number $\pm \frac{1}{2}$.‡

The total angular momentum thus appears as a resultant to which the spin contributes only one component. The other component (which is obtained by geometrical subtraction) appears to be characterised by another quantum number l , which is shown by theoretical considerations to change by ± 1 during every quantum change of the atom. Consideration of the optical spectrum shows that it corresponds to the so-called subordinate quantum number introduced by Sommerfeld in 1915, to account for the optical spectra. Quantum

* *Naturwissenschaften*, **13**, (1925), p. 953.

† *Zeitschr. f. Phys.* **37**, (1926), p. 263.

‡ For two electrons, therefore, the angular momentum corresponding to their spin totals ± 1 or 0, for three electrons $\pm \frac{3}{2}$ or $\pm \frac{1}{2}$, for four electrons ± 2 , ± 1 or 0, etc.

mechanics shows that the subordinate quantum number forms a series of whole numbers, never negative,* and that the maximum value attained by the subordinate quantum number l corresponding to a principal quantum number n is always one less than n , so that

$$l_{\max} + 1 = n \dots \dots \dots \quad (131)$$

For a given principal quantum number n , there are therefore n possible values of l , namely,

$$0, 1, 2 \dots (n - 1).$$

The key to the understanding of the periodic system was discovered by Pauli † in his principle, which states that in a single atom two electrons can never coincide in all four quantum numbers (principal, subordinate, inner and magnetic). In order to elucidate Pauli's principle, let us imagine the planetary electrons in an atom divided into groups characterised by a given value of the principal quantum number (I, II, III, IV, etc.). Within these groups, sub-groups may be distinguished, which are again characterised by a given value of the subordinate quantum number. If we add the value of the subordinate number as a suffix to the roman numeral representing the principal quantum number, the following groups are shown by equation (131) to be possible :

$$I_0; II_0, II_1; III_0, III_1, III_2; IV_0, IV_1, IV_2, IV_3; V_0, \text{etc.}$$

Considering in general a sub-group corresponding to the subordinate quantum number l , and disregarding for the moment the special case where $l = 0$, the corresponding

* The significance of the subsidiary quantum number is most readily seen in the case of the optical spectra of the alkali metals, where four chief groups of optical spectral terms are to be distinguished, corresponding to the values 0, 1, 2 and 3 of l . The duplex nature of the inner quantum number j explains the fact that the terms are doublet terms, with the exception of those corresponding to $l = 0$, which are always simple terms for which only a single value of j is possible. The relationships are considerably more complicated in the case of the other elements.

† *Zeitschr. f. Phys.* **31**, (1925), p. 765.

values of the inner quantum number of an electron are seen to be

$$\left. \begin{array}{l} j_1 = l - \frac{1}{2} \\ j_2 = l + \frac{1}{2} \end{array} \right\}$$

Moreover, as already mentioned, the magnetic quantum number, m , may have all the values between $-j$ and $+j$, which differ by unity. The number of possible values of the magnetic quantum number is therefore $(2j + 1)$, or $2l$ for j_1 , while for j_2 it is $(2j_2 + 1)$ or $(2l + 2)$; the total number is thus $(4l + 2)$. It will readily be seen that this expression is also true for $l = 0$, since j_1 , then disappears and $j_2 = +\frac{1}{2}$. The only possible values of the magnetic quantum number are then $-\frac{1}{2}$ and $+\frac{1}{2}$; the number of possible values is accordingly $(4 \times 0) + 2 = 2$.

According to Pauli's principle the maximum number of electrons which can exist in a sub-group of subordinate quantum number l is therefore

$$Z_{\max} = 4l + 2 \quad \dots \dots \dots \quad (132)$$

This gives :

$$\begin{aligned} & 2 \text{ for } l = 0 \\ & 6 \text{ for } l = 1 \\ & 10 \text{ for } l = 2 \\ & 14 \text{ for } l = 3 \\ & 18 \text{ for } l = 4, \end{aligned}$$

and so on. If, for example, we represent by III_{01} a three-quantum group which does not contain all the three possible sub-groups ($l = 0$, $l = 1$, $l = 2$), but only the first two, the following numbers of electrons are obtained, where X is any given principal quantum number :

$$\left. \begin{array}{l} X_0 = 2 \\ X_{01} = 8 \\ X_{012} = 18 \\ X_{0123} = 32, \end{array} \right\} \quad \dots \dots \dots \quad (133)$$

and so on. These numbers are, however, exactly the same as those which represent the lengths of the various periods.

The following scheme * is thus obtained for the inert gases ending the periods, whose atomic numbers are 2, 10, 18, 36, 54 and 86.

$$\begin{array}{ll}
 \text{Helium} & = \text{I}_0 \\
 \text{Neon} & = \text{I}_0 + \text{II}_{01} \\
 \text{Argon} & = \text{I}_0 + \text{II}_{01} + \text{III}_{01} \\
 \text{Krypton} & = \text{I}_0 + \text{II}_{01} + \text{III}_{012} + \text{IV}_{01} \\
 \text{Xenon} & = \text{I}_0 + \text{II}_{01} + \text{III}_{012} + \text{IV}_{012} + \text{V}_{01} \\
 \text{Emanation} & = \text{I}_0 + \text{II}_{01} + \text{III}_{012} + \text{IV}_{0123} \\
 & \quad + \text{V}_{012} + \text{VI}_{01}
 \end{array} \quad \left. \right\} . \quad (134)$$

If we insert the numerical values for the symbols on the right-hand side according to formula (133), we obtain

$$\begin{array}{ll}
 2 & = 2 \\
 2 + 8 & = 10 \\
 2 + 8 + 8 & = 18 \\
 2 + 8 + 18 + 8 & = 36 \\
 2 + 8 + 18 + 18 + 8 & = 54 \\
 2 + 8 + 18 + 32 + 18 + 8 & = 86
 \end{array} \quad \left. \right\}$$

The essentials of the scheme (134) representing the building up of the periodic system were given by Stoner † as early as 1924, being based on some rather earlier ideas of Bohr.‡ The more fundamental basis of the "arithmetic" of the periodic system was first discovered through the principle of Pauli.

* It may be mentioned here in passing that this scheme shows that the building up of the periodic system is characterised by a completion of inner electron groups. The three-quantum group is not completed until the fourth period, the four-quantum group is completed in the fifth and sixth periods, while the completion of the five-quantum group is continued in the sixth period without reaching finality.

† E. C. Stoner, *Phil. Mag.* **48**, (1924), p. 719.

‡ N. Bohr, *Zeitschr. f. Phys.* **9**, (1922), p. 1.

CHAPTER XIII

THE QUANTUM STATISTICS OF BOSE

THE bridging of the gap between corpuscles and waves, *i.e.*, between matter and light, introduced by the latest developments of physics, has also become of the greatest importance for the problems of statistical physics. These problems were formerly separated into two sharply differentiated groups. The one limited itself to matter, the other to light, in the broadest sense of the word. The statistical physics of material particles had been brought to a high degree of perfection by the middle of the nineteenth century. In the domain of light waves, statistical considerations have been made possible, on the one hand by means of the conception of characteristic vibrations,* and on the other by the idea of energy elements ($h\nu$) and light quanta. As soon as it was found by physicists that light quanta must be regarded as possessing momentum just like material particles, the idea of transferring the methods and results of the first group of problems to the second group suggested itself. The converse possibility was also opened up by the hypothesis of material waves.

The first notable attempt to solve a problem in the radiation theory by the methods of the gas theory concerned the fundamental question of how the spectral distribution of the energy of electro-magnetic waves in a cavity depends on the temperature. The solution of this problem had been reached in 1900 with the discovery of the famous radiation law, founded by Planck, on the basis of his hypothesis of the elementary quantum of action. The idea now suggested itself of deducing Planck's radiation

* See the remarks on the Rayleigh-Jeans principle in Chapter III.

law by regarding the radiation filling the cavity as a "light-quantum gas," so to speak, in which the possible values of the momentum should be distributed over the various individuals composing the gas, just as they are in a "material" gas; remembering, of course, that in a "material" gas the momentum is the product of molecular mass and molecular velocity, while in cavity radiation it is given by the value of $h\nu$ divided by the velocity of light.

Planck had deduced the following value for the "specific radiation density," u_ν :

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \quad \dots \quad (135)$$

where c is the velocity of light, T the absolute temperature and k the Boltzmann constant,† which, when multiplied by $3/2T$ gives the mean kinetic energy of a monatomic molecule at temperature T . The specific radiation density u_ν , which depends on the frequency and the temperature, represents the distribution of the total energy of radiation η per unit volume among the various spectral regions, so that

$$\eta = \int u_\nu d\nu.$$

It may be remarked in passing that, if u_ν is multiplied by $c/4$, the product is the so-called specific emissive power ‡ of

† The Boltzmann constant k represents the universal proportionality between the entropy S and the natural logarithm of the statistical probability W^* . The following relation therefore exists

$$S = k \ln W^*.$$

The numerical value of the Boltzmann constant is $1.372 \cdot 10^{-16}$ erg/degree.

‡ By the emissive power of a black body is meant the energy radiated by unit area in unit time. If this emissive power is divided up over the spectrum, *i.e.*, equated to $\int K_\nu d\nu$, we find by multiplying equation (134) by $c/4$

$$K_\nu = \frac{2\pi h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{kT}} - 1}.$$

a black body for the spectral region from ν to $\nu + d\nu$ at temperature T.

Now all statistical considerations in the kinetic theory of gases are based upon the conception of the statistical probability of a given distribution of states. By this probability is meant the number of complexions corresponding with the given distribution. Let us consider, for example, a system of N individuals, and arrange the possible states of the individuals (at first with an arbitrary limitation) in a numbered series. Let N_1 be the number of individuals in the first state, N_2 in the second state, and, in general N_i in the i th state, so that

$$\sum_i N_i = N \quad \dots \quad \dots \quad \dots \quad (136)$$

Then a new complexion arises when two individuals in different states change places ; on the other hand, no new complexion arises when two individuals in the same state are interchanged. If, for instance, we distinguish two states with three individuals (a, b, c), then for one distribution of states :

$$N_1 = 2, N_2 = 1,$$

If the emissive power is referred to a range of wavelengths (λ to $\lambda + d\lambda$) instead of a frequency range in the usual manner, the last equation, since $c = \lambda\nu$, becomes the well-known Planck formula

$$K_\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{\frac{ch}{k\lambda T}} - 1}.$$

When λT is small, we obtain the Wien law, which holds only for the ultra violet or for low temperatures

$$K_\lambda = \frac{2\pi hc^2}{\lambda^5} e^{-\frac{ch}{k\lambda T}}.$$

When λT is large, the expression reduces to the Rayleigh radiation law, valid only for the infra red or for high temperatures

$$K_\lambda = \frac{2\pi ckT}{\lambda^4}.$$

The laws of Wien and Rayleigh, which have only a limited range of application, were both known before the development of the generally-applicable Planck law.

three complexions are possible, according to the following table :

State 1.	State 2.
$a\ b$	c
$a\ c$	b
$b\ c$	a

Similarly, there are three complexions for the distribution $N_1 = 1, N_2 = 2$. On the other hand, for the distribution $N_1 = 3, N_2 = 0$, only one complexion is possible, and similarly for $N_1 = 0, N_2 = 3$.

The statistical probability, which must always be a positive integer, is therefore obviously determined by the number of permutations of N individuals, when all permutations are neglected which consist in the interchange of two individuals in the same state. The total number of possible permutations of N individuals is $N!$ (factorial N), where the symbol $N!$ represents the product $[1. 2. 3 \dots (N-1).N]$. The number of possible permutations formed by interchanging the various individuals in the first state is $N_1!$, and so on. We therefore obtain the statistical probability of a given distribution of states by first dividing $N!$ by $N_1!$, since all the combinations formed by interchanging the individuals within the first sub-group only represent one complexion (and not $N_1!$ complexions). We must then divide by $N_2!$, etc. The statistical probability, represented by W^* , is therefore given by the expression :

$$W^* = \frac{N!}{N_1! N_2! \dots N_i! \dots} \dots \dots \dots \quad (137)$$

It was shown in 1924 by the Indian physicist, Bose,† that from the idea of the "light-quantum gas" it was possible to deduce the fundamental Planck formula by imagining the momentum space of a quantum gas of unit volume ‡

† S. N. Bose, *Zeitschr. f. Phys.* **26**, (1924), p. 178, and **27**, (1925), p. 384.

‡ Since the energy in a cavity of unit volume is the same as the energy density.

to be composed † of cells of size \hbar^3 , and then defining the statistical probability in a manner which differs from the classical theory.

The difference between classical statistics and the method of Bose may be explained from the example already discussed, where only two states and three individuals are considered. In this case, classical statistics distinguished four different distributions of states, each of different "weight" (when there are m possible complexions, so that $W^* = m$, the "weight" is said to be m). These four possible distributions, in the case considered, are :

$N_1 = 3, N_2 = 0$	Weight = 1
$N_1 = 2, N_2 = 1$	Weight = 3
$N_1 = 1, N_2 = 2$	Weight = 3
$N_1 = 0, N_2 = 3$	Weight = 1

Contrary to the classical idea, Bose's statistics ascribes only unit weight to all these distributions. All distributions of the individuals among the different states are, according to Bose, equally probable, exactly as in classical statistics all the individual complexions (e.g., ab ; c or ac ; b or bc ; a) have the same probability. Accordingly, in Bose's statistics we must start, not from the distribution of individuals among various states, but from the distribution of states or cells over the various possible "degrees of occupation" (i.e., number of states occupied by a given number of individuals). If N individuals are divided among Z states, this distribution is characterised in classical statistics by the Z numbers, $N_1, N_2 \dots N_i \dots$, which show how many individuals exist in each state. In Bose's statistics the distribution is given by $(N + 1)$ numbers, namely, $Z_0, Z_1 \dots Z_j \dots$, which show how many states or cells are occupied by 0, how many by 1, and how many by j individuals; therefore

$$\sum_j Z_j = Z \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (138)$$

† See the remarks at the end of Chapter III.

The statistical probability is therefore given on Bose's theory, in contrast to the classical theory, by

$$W = \frac{Z!}{Z_0! Z_1! \dots Z_j! \dots} \dots \dots \quad (139)$$

If, for example, we consider in the special case discussed earlier, where $N = 3$, $Z = 2$, the particular distribution where two individuals are in the first and one in the second state, equation (137) shows that the classical probability (corresponding with the " weight ") is

$$W^* = \frac{3!}{2! 1!} = 3.$$

The probability on Bose's theory, on the other hand, is given by equation (139) as

$$W = \frac{2!}{1! 1!} = 2,$$

since in the given distribution no cell contains 0 individuals, one contains 1, one contains 2, and none contains 3.

The agreement between equations (137) and (139), and also that between equations (136) and (138), justifies us in transferring the fundamental results of classical statistics to Bose's method, applying quantities which refer in the classical theory to an individual in the i th state to a cell in Bose's theory, which contains i individuals. Now one of the fundamental formulæ of the classical kinetic theory of heat is as follows.† If an amount of energy E is distributed among N individuals at a temperature T , and if ϵ_i is the energy of an individual in the state corresponding to the index i , then in statistical equilibrium the following relation must hold :

$$\frac{E}{N} = \frac{\sum \epsilon_i e^{-\frac{\epsilon_i}{kT}}}{\sum e^{-\frac{\epsilon_i}{kT}}} \dots \dots \dots \quad (140)$$

In using this equation in the problem of the " light-

† See, for example, the author's "Introduction to Theoretical Physics" (Constable, London; Van Nostrand, New York, 1925), Vol. II., § 132, equation (16) and § 142, equation (2).

quantum gas," we must at first limit ourselves to a consideration of those light quanta in the "gas" whose frequency lies within the small interval ν to $\nu + d\nu$. According to what has been said, ϵ_i , in Bose's statistics, means the energy within a cell containing i light quanta of frequency ν . Therefore

$$\epsilon_i = ih\nu \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (141)$$

and consequently

$$\sum e^{-\frac{\epsilon_i}{kT}} = \sum_{n=0}^{n=Z} e^{-\frac{n h\nu}{kT}}.$$

Now from the well-known summation rule for infinite geometric series (when $y < 1$):

$$1 + y + y^2 + y^3 + \dots = \frac{1}{1 - y}.$$

Since the series is necessarily strongly convergent * and therefore the upper limit of the sum may be taken at infinity instead of Z :

$$\sum e^{-\frac{\epsilon_i}{kT}} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} \quad \dots \quad \dots \quad \dots \quad \dots \quad (142)$$

If we differentiate this equation partially with respect to temperature, and then multiply both sides by kT^2 , we obtain

$$\sum \epsilon_i e^{-\frac{\epsilon_i}{kT}} = \frac{h\nu e^{-\frac{h\nu}{kT}}}{\left(1 - e^{-\frac{h\nu}{kT}}\right)^2} \quad \dots \quad \dots \quad \dots \quad \dots \quad (143)$$

We must now divide equation (143) by equation (142). The left-hand side must then, according to equation (140), represent the mean value of the energy belonging to a single cell. This mean value, which will be represented by $\bar{\epsilon}$, is therefore

$$\bar{\epsilon} = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (144)$$

* The quotient $h\nu/kT$ is of the order 50 for visible light at room temperature.

Let us now consider the "momentum space" representing the momenta of the light quanta of all frequencies contained in the "gas," remembering that the momentum of a light quantum is given by

$$p = \frac{h\nu}{c};$$

All the cells in the momentum space which correspond to a frequency between ν and $\nu + d\nu$ must lie in the spherical volume bounded by the two radii :

$$r_1 = \frac{h}{c}\nu, r_2 = \frac{h}{c}(\nu + d\nu).$$

The volume of this spherical shell is

$$4\pi r_1^2(r_2 - r_1) \text{ or } 4\pi \frac{h^3}{c^3} \nu^2 d\nu.$$

Since each cell in the momentum space has, on our original assumption, the size h^3 , the number of cells in this spherical shell is $Zd\nu$, where

$$Z = \frac{4\pi\nu^2}{c^3} \dots \dots \dots \quad (145)$$

Further, if we distinguish between two states of polarisation at right angles to one another, on account of the transverse nature of light waves,

$$2Z\bar{\epsilon} = u, \dots \dots \dots \quad (146)$$

and Planck's formula (equation (135)) is therefore obtained. It may be mentioned that the Planck formula may also be deduced from the Rayleigh-Jeans principle (see Chapter III.) by ascribing to each characteristic vibration an energy which is an integral multiple of $(h\nu)$.* If this multiple is n , instead of the n -quantum characteristic vibrations, Bose's theory deals with cells containing n light quanta.

De Broglie's theory of material waves suggested to

* See, for example, the derivation given in 1921 by the author in the first edition of his "Einführung in die theoretische Physik," equation (6), § 106.

Einstein * the possibility of developing a gas theory whose formulæ should be deducible from Bose's statistics in the same way as those of the earlier gas theory are deducible from classical statistics. The differences between Einstein's gas theory and the classical theory consist essentially in the fact that in the classical formulæ containing the expression, $e^{-\frac{\epsilon}{kT}}$, this expression must be replaced by the following more complicated term :

$$\frac{1}{Be^{\frac{\epsilon}{kT}} - 1} \quad \dots \dots \quad (147)$$

where B is a function of temperature.

The differences between this and the older formula are without significance until extremely low temperatures are reached, at which perfect gases begin to show the phenomenon of "degradation," which is inexplicable on the classical theory. Recently, however, the Einstein gas theory has receded into the background in comparison with another gas theory developed by the Italian physicist, Fermi, on the basis of Pauli's principle.

* A. Einstein, *Sitz. Ber. der Berlin, Akad.* (1924), p. 261; (1925), pp. 3, 18.

CHAPTER XIV

THE STATISTICS OF FERMI

PAULI's principle gives the number of individuals in the electron groups forming the planetary systems of the atoms ; the theory of material waves, when applied to a gas enclosed in a vessel, leads necessarily to a quantisation of the translational energy, and, finally, Bose's statistics are based on the consideration of the numbers of individuals contained in certain "cells" of the momentum space. All this suggested the additional application of Pauli's principle to the statistical theory of gases. As a result of working out this idea, there appeared, in 1926, Fermi's theory of gas degradation,* founded on the assumption that, in a gas, at most a single molecule possessing predetermined quantum numbers can be present.

We will disregard the internal movements of the molecules, thus limiting ourselves to monatomic molecules, which in addition may be assumed to exist entirely in the normal state.† We must then evidently (as in the cases considered in Chapter III.) ascribe three quantum numbers (n_1, n_2, n_3) to each molecule, corresponding to the three degrees of freedom ; the energy can then be expressed as follows :

$$\epsilon_n = h\nu(n_1 + n_2 + n_3) = nh\nu \dots \quad (148)$$

where ν is a fundamental frequency. The question now arises, by how many complexions can the energy, $nh\nu$, be realised for a single molecule. This number of complexions, which we will call s , is evidently identical with

* E. Fermi, *Zeitschr. f. Phys.* **36**, (1926), p. 902.

† It must further be assumed that the normal state cannot be magnetically resolved.

the number of solutions possessed by the indeterminate equation :

$$n_1 + n_2 + n_3 = n$$

for integral values of n_1, n_2, n_3 , these values all being positive or zero. In order to determine the number of solutions, we must remember that, if n_1 and n_2 are arbitrarily chosen, the value of n_3 is fixed. Since n_2 may have the value 0, but can never be negative, there are $(n + 1)$ possibilities for n_2 when $n_1 = 0$; n possibilities when $n_1 = 1$; two possibilities ($n_2 = 1$ or $n_2 = 0$) when $n_1 = (n - 1)$, and only a single possibility ($n_2 = 0$) when $n_1 = n$. We therefore find

$$s = (n + 1) + n + (n - 1) + \dots + 2 + 1,$$

or, since the sum of all the positive integers from 1 to x is known to be $x(x + 1)/2$,

$$s = \frac{(n + 1)(n + 2)}{2} \dots \dots \dots \quad (149)$$

On Fermi's assumption, therefore, the maximum possible numbers of molecules in a gas possessing various amounts of energy are as follows :

Energy	0	Maximum number of molecules	1
„	$h\nu$	„	3
„	$2h\nu$	„	6
„	$3h\nu$	„	10
„	$4h\nu$	„	15

and so on. As an example, the energy of a gas made up of only 40 molecules could never fall below

$(1 \times 0) + (3 \times 1) + (6 \times 2) + (10 \times 3) + (15 \times 4) + (5 \times 5)$ or $130 h\nu$. Application of Pauli's principle to statistics thus leads to the conclusion that, even at the absolute zero, a gas must possess some energy. The distribution of energy among the molecules must therefore show an arrangement, analogous to the "shell" structure of the systems of planetary electrons in the atom.*

* The numbers of the complete electron groups, 2, 8, 18, 32, etc., have their counterpart in Fermi's statistics in the numbers 1, 3, 6, 10, 15, etc.

A given distribution of states may again be described by the numbers N_i , representing the number of molecules whose energy equals $ih\nu$. Contrary to the classical theory, however, the numbers N_i in Fermi's theory are subject to the limitation that

$$N_i \leq Q_i \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (150)$$

where for the sake of brevity,

$$Q_i = \frac{(i+1)(i+2)}{2} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (151)$$

If now there are in the gas N_i molecules with a total quantum number i (i.e., with energy $ih\nu$), the maximum possible number of such molecules being Q_i , an elementary rule of combination leads, when only molecules of total quantum number i are considered, to the statistical probability * :

$$\binom{Q_i}{N_i}.$$

On Fermi's theory, therefore, the statistical probability, W_F , for the total distribution is

$$W_F = \binom{Q_0}{N_0} \binom{Q_1}{N_1} \binom{Q_2}{N_2} \dots \binom{Q_i}{N_i} \dots \quad (152)$$

$$= \prod \binom{Q_i}{N_i}.$$

On the basis of this formula, calculations may be carried out in an analogous manner to those in the classical statistics or Bose's method. The results arrived at are quite complicated, but they assume a simpler form for the two limiting cases of weak and strong degradation. Now the equation of state of a perfect gas according to the classical theory is as follows :

$$p = NkT \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (153)$$

where p is the pressure and N the number of molecules

* In the usual manner $\binom{n}{k} = \frac{n(n-1)(n-2)\dots(n-k+1)}{1 \cdot 2 \cdot 3 \dots k}$.

per unit volume. For the limiting case of slight degradation, Fermi's theory gives an equation of state of the form :

$$p = NkT \left[1 + \frac{1}{16} \frac{h^3 N}{(\pi m k T)^{\frac{3}{2}}} \right], \quad \dots \quad (154)$$

where m is the molecular mass. From this equation the pressure is greater than that given by the classical theory.* For helium at 5° abs. and a pressure of 10 atmospheres the difference amounts to roughly 15 per cent.

For the limiting case of strong degradation, Fermi's theory leads to the equation :

$$p = \frac{1}{20} \left(\frac{6}{\pi} \right)^{\frac{2}{3}} \frac{h^2 N^{\frac{5}{3}}}{m} + \frac{\frac{4}{3} \frac{8}{\pi^{\frac{2}{3}}}}{\frac{5}{3^{\frac{2}{3}}}} \frac{m N^{\frac{1}{3}} k^2 T^2}{h^2} + \dots \quad (155)$$

From this formula it is seen that, even when $T = 0$, the gas exerts a certain pressure, and that besides a zero point energy there must also be a zero point pressure. The formula deduced by Fermi for the specific heat (at constant volume) in the case of great degradation should also be noted, namely,

$$c_v = \frac{\frac{4}{3} \frac{8}{\pi^{\frac{2}{3}}}}{\frac{2}{3^{\frac{2}{3}}}} \frac{m k^2 T}{h^2 N^{\frac{2}{3}}} + \dots \quad \dots \quad (156)$$

* The differences between Fermi's gas theory and the classical theory and that of Einstein may be roughly described by saying that, instead of the classical expression

$$e^{-\frac{\epsilon}{kT}}$$

or, in Einstein's theory (cf. equation (147))

$$\frac{1}{B e^{\frac{\epsilon}{kT}} - 1},$$

the expression

$$\frac{1}{A e^{\frac{\epsilon}{kT}} + 1}$$

is used in Fermi's theory. B represents a function of the temperature, as does A , and further, as was shown by Heitler and Pauli,

$$\ln A = -\frac{\mu}{kT},$$

where μ represents in Gibbs' notation the thermodynamic potential expressed in unit mass of the electrons.

The specific heat thus vanishes at the absolute zero, while otherwise in the case of great degradation it is proportional to the absolute temperature.*

A very important field of application of Fermi's statistics is the electronic theory of metals, as was found by Sommerfeld † in 1927. The idea that the free electrons in a metal, which are the cause of its conductivity for electricity and heat, behave like a gas, meets with insuperable difficulties from the standpoint of classical statistics in spite of its otherwise promising appearance. According to classical statistics, each free electron at temperature T , like a monatomic molecule, possesses a kinetic energy amounting to $3kT/2$. The free electrons must therefore on the classical theory contribute an appreciable amount to the specific heat of metals. This result is, however, obviously contrary to actual experience.

Sommerfeld showed, nevertheless, that the difficulty disappears when the method of Fermi is applied to the free electrons. Since the mass of an electron is about 1,800 times smaller than that of the lightest atom, the electron gas must, on Fermi's theory, exist at room temperature in a state of complete degradation. It actually follows from equation (154), in the limiting case of weak degradation, that, at the same temperature and considering an equal number of particles, the correction term for the electron gas is some hundred thousand times greater than for helium gas. In a state of great degradation, on the other hand, according to equation (156), the specific heat is proportional to the mass, and therefore the contribution of the electrons is relatively insignificant

* It may be mentioned that Fermi's theory also gives the Stern-Tetrode value for the absolute entropy of a gas

$$S = Nk \left[\frac{3}{2} \ln T - \ln N + \ln \frac{(2\pi m)^{\frac{3}{2}} k^{\frac{3}{2}} e^{\frac{5}{2}}}{h^3} \right]$$

(where e is the base of the natural logarithms).

† A. Sommerfeld, "Zur Elektronentheorie der Metalle," *Naturwissenschaften*, **15**, (1927), p. 825. *Zeitschr. f. Phys.* **47**, 1928, p. 1.

compared with the specific heat of the metal, on account of the small mass of the electrons.*

Application of Fermi's statistics to the electron gas leads at once, as Sommerfeld showed, to the well-known Wiedemann-Franz law, according to which the relation between the heat conductivity and the electrical conductivity of a metal is always proportional to the absolute temperature. A numerical factor occurring in this law was estimated in the original electronic theory of metals as 3, later in a more exact calculation on the classical statistical theory as 2, while on the basis of Fermi's

statistics it is given as $\frac{1}{3}\pi^2$ or approximately 3.3. The

last of the three values is that which agrees most nearly with the results of measurement. Sommerfeld has also applied Fermi's theory with good results to the theory of contact potentials, as well as to the Peltier and Thomson effects.† He was able to show that Fermi's theory gives values of the correct order of magnitude for these effects and their variation with temperature. A particular triumph for the new theory lies in the fact that, unlike earlier theories, no special hypotheses as to the mutual action between free electrons and the atomic residues of the metals are necessary.

* While on the classical theory the contribution of the free electrons towards the specific heat would be $3R/2$, when R is the gas constant and the specific heat is referred to the mol., according to Fermi's statistics the contribution at room temperature would only be about $R/100$.

† The Peltier effect, as is well known, consists in the fact that when a current is allowed to flow in a circuit composed of two metals, heating occurs at one junction and cooling at the other. William Thomson further showed that, even in one and the same metal, thermal effects occur when a current flows between two points at different temperatures.

CHAPTER XV

FURTHER APPLICATIONS OF QUANTUM MECHANICS

EVEN in the first two years since its foundation, the new quantum theory has found a host of important applications. A few of these have already been discussed briefly in the earlier chapters, such as the theories of the hydrogen atom and the Stark effect, quantisation of the atom and the periodic system, gas degradation and the free electrons of metals. Of the considerable number of other applications, only the most important can be mentioned here.

First of all, we arrive at a very remarkable result on the basis of equations (127) already given. In the discussion of these equations, as was mentioned at the time, we can distinguish between two different kinds of quantum change, according to whether, during the change, the angular momentum of the system, symmetrical about its axis, changes or remains unaltered. In the first case the expression $(U_n - U_m)$ in the last of the three equations (127) differs from zero, so that

$$q_z(n, m) = 0.$$

Since the individual terms of a matrix represent products of amplitudes and exponential expressions, the vanishing of $q_z(n, m)$ can only mean that the elementary light wave resulting from the quantum change in question has no component of vibration in the direction of the z -axis. Further, from the first two equations (127) it is seen that the x -axis has no preference over the y -axis, or the reverse, so that circular vibrations at right angles to the axis of symmetry of the system are obviously indicated.*

* The axis of symmetry of the system was chosen as the z -axis.

If, on the other hand, the angular momentum remains unaltered during the quantum change, the left-hand, and therefore also the right-hand sides of the equations are zero, and $q_y(n, m)$ and $q_x(n, m)$ vanish. The light vibrations then take place parallel to the axis of symmetry. In the first case, where the angular momentum changes by $\pm h/2\pi$ according to equation (128), the light is therefore circularly polarised, while in the second case, where the angular momentum is unaltered, it is plane polarised. This so-called polarisation rule, together with the selection principle according to which the value of $2\pi U/h$ can only change by ± 1 or 0, was deduced by Rubinowicz as early as 1918. Both principles are given by quantum mechanics, unlike the older theories, without the necessity of introducing any further hypothesis.

The method of perturbations, already mentioned in connection with Schrödinger's mechanics of characteristic values, has been also developed from other points of view in matrix mechanics, and one of its most important results is a theory of dispersion.* The starting point is the question of what perturbations are suffered by the terms in the co-ordinate matrix of an electron when the latter is placed in a periodically varying electric field, such as a light wave.

If F_0 represents the amplitude of the electric field strength, and ν the frequency of its periodic variation, and if \mathbf{q}_0 and \mathbf{p}_0 are the co-ordinate and momentum matrices in the undisturbed state, and if $\nu_0(n, m)$ represents the transition frequencies of the atom in question, then application of matrix mechanics gives for \mathbf{q}_1 , the perturbation of the co-ordinate matrix :

$$q_1(n, m) = \frac{F_0 e}{4\pi i \hbar \mu} \sum_k \frac{q_0(n, k) p_0(k, m) - p_0(n, k) q_0(k, m)}{[\nu_0(n, k) + \nu][\nu_0(k, m) + \nu]} . \quad (157)$$

where e and μ represent as usual, the electric charge and the

* See Born, "Problems of Atomic Dynamics" (Cambridge, U.S.A., 1926), Part I., Lecture 14.

mass. For the diagonal terms of the co-ordinate matrix the last equation assumes the simpler form :

$$q_1(n, n) = -\frac{F_0 e}{4\pi i \hbar \mu} \sum_k \frac{q_0(n, k)p_0(k, n) - p_0(n, k)q_0(k, n)}{\nu_0^2(n, k) - \nu^2}. \quad (158)$$

Multiplication of the perturbation of the co-ordinate matrix by the charge gives the moment of the polarisation produced by the electric field, and hence, by the usual methods of the electromagnetic theory of light, the relation between colour and refractive index.

Equation (158) is an extension of a dispersion formula suggested in 1921 by Ladenburg,* and later improved by Kramers † and Heisenberg. ‡ In contrast to the older dispersion formulæ which connected the light frequency with the vibration number of the electrical moment, Ladenburg's formula was the first in which the frequency of the quantum changes in the atom was used instead of the above vibration number. Equation (157) also leads to a further result opposed to the classical theory, namely, that the scattered light need not coincide in frequency with the incident light, but that combination frequencies such as $\nu \pm \nu_0(n, k)$ may also occur. So far it has not been possible to make optical observations of this phenomenon, first postulated by Smekal. §

In the theory of the Zeeman effect, Heisenberg and Jordan ‖ succeeded by means of matrix mechanics in deducing Landé's resolution formula and making it more exact. The displacement suffered by a spectral term when resolution occurs in a magnetic field is, as has been long known :

$$\Delta\nu = \frac{e}{4\pi c \mu} zH, \quad \dots \dots \quad (159)$$

where once more e and μ are the charge and mass of the

* R. Ladenburg, *Zeitschr. f. Phys.* **4**, (1921), p. 451.

† H. A. Kramers, *Nature*, **113**, (1924), p. 673.

‡ H. A. Kramers and W. Heisenberg, *Zeitschr. f. Phys.* **31**, (1925), p. 681.

§ A. Smekal, *Naturwissenschaften*, **11**, (1923), p. 873.

|| See Born, "Problems of Atomic Dynamics," Part I., Lecture 18.

electron, H is the magnetic field strength and z is a number. Now Landé showed,* in 1923 that, in a weak magnetic field

$$z = mg \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (160)$$

where m is the magnetic quantum number and

$$g = 1 + \frac{j(j+1) + r(r+1) - l(l+1)}{2j(j+1)} \quad \dots \quad (161)$$

In equation (161), as in Chapter XII., l represents the subordinate quantum number, which may have all integral values from zero up to one less than the principal quantum number; r is the quantum number which measures the angular momentum due to the spinning motion of the electrons, and j is the inner quantum number. Quantum mechanics has provided a sound foundation for this formula of Landé's, which enables the resolution phenomena to be accurately calculated.

An explanation of the phenomenon known as the Paschen-Back effect has also been found on the basis of quantum mechanics. This effect is due to the transition with increasing magnetic field strength from the so-called anomalous Zeeman effect described by Landé's formula to the "normal" Zeeman effect already explained by the classical theory.† The transition from the anomalous to the normal effect is explained by the fact that the conditions for the validity of the Landé resolution formula are only fulfilled so long as the mutual action between the motions corresponding to the quantum numbers l and r is not perturbed by the magnetic field.

Although in the case of Landé's formula and the Paschen-Back effect quantum mechanics has merely established more exactly the conclusions of the earlier theory, it has yielded results differing from those of the

* A. Landé, *Zeitschr. f. Phys.* **15**, (1923), p. 189.

† The classical theory of the normal Zeeman effect was developed in 1896 by H. A. Lorentz, independently of the quantum theory and prior to its foundation. Equation (159) was deduced, with the numerical factor $z = \pm 1$.

earlier theory and in closer agreement with experiment in the case of the intensity relations of the Zeeman components of spectral lines. In a previous chapter (Chapter XII.) it has already been pointed out that only those quantum changes are possible in which j either alters by ± 1 or remains unchanged; the same is also true for the magnetic quantum number m . For a given value of principal and subordinate quantum numbers there are therefore nine transitions possible.

Let us consider first the three transitions in which the inner quantum number rises by one; these may be represented by the following symbols :

$$\begin{aligned}(j, m) &\longrightarrow (j + 1, m + 1) \\ (j, m + 1) &\longrightarrow (j + 1, m) \\ (j, m) &\longrightarrow (j + 1, m).\end{aligned}$$

The following values are then obtained for the intensity relationships of the corresponding lines by the application of quantum mechanics * :

$$[(j + m + 2)(j + m + 1)] : [(j - m + 1)(j - m)] : [(j + 1)^2 - m^2].$$

The three transitions in which j remains unaltered may be represented as follows :

$$\begin{aligned}(j, m - 1) &\longrightarrow (j, m) \\ (j, m) &\longrightarrow (j, m - 1) \\ (j, m) &\longrightarrow (j, m).\end{aligned}$$

For these transitions the intensity relationships are :

$$[j(j + 1) - m(m - 1)] : [j(j + 1) - m(m - 1)] : m^2.$$

Finally, we may consider the processes in which j diminishes by 1, as follows :

$$\begin{aligned}(j, m - 1) &\longrightarrow (j - 1, m) \\ (j, m) &\longrightarrow (j - 1, m - 1) \\ (j, m) &\longrightarrow (j - 1, m).\end{aligned}$$

* See Born, "Problems of Atomic Dynamics," Part I., Lecture 17.
W.M.

For these transitions quantum mechanics gives the following intensity relationships :

$$[(j-m)(j-m+1)] : [(j+m)(j+m-1)] : [j^2 - m^2].$$

In the theory of the neutral helium atom the older quantum theory failed completely, although the helium atom is the next simplest atom after that of hydrogen. The fundamental problem was the calculation of the ionisation potential of helium ; this, when multiplied by the electronic charge gives the work necessary to remove an electron from the neutral helium atom. All previous theoretical investigations gave values for this potential which could not be brought into agreement with the results of experiment, until Kellner * was able, on the basis of Schrödinger's theory, to deduce a value in good agreement with fact.

Both the Compton effect and the photoelectric effect have been subjected to many investigations by the methods of the new theory. Dirac † treated the Compton effect from the standpoint of q -number mechanics, and succeeded in solving satisfactorily the problem of the relation between the direction and the frequency and intensity of the scattered radiation during the scattering of X-rays by loosely bound electrons. Dirac obtained the same expression for the frequency as had previously been obtained by Compton and Debye on the light quantum hypothesis. The expression obtained by Dirac for the intensity differed somewhat from the older theory, but agreed better than the latter with experiment. The Compton effect was also treated by Gordon ‡ on the basis of Schrödinger's theory, and the relativistic wave equation for the case of the single electron problem was deduced.

Furthermore, Wentzel § and Beck || have investigated the behaviour of an atom under the action of a light wave

* G. W. Kellner, *Zeitschr. f. Phys.* **44**, (1927), p. 91.

† P. A. M. Dirac, *Proc. Roy. Soc. (A)* **111**, (1926), p. 405.

‡ W. Gordon, *Zeitschr. f. Phys.* **40**, (1926), p. 117.

§ G. Wentzel, *Zeitschr. f. Phys.* **40**, (1926), p. 574; **41**, (1927), p. 828.

|| G. Beck, *Zeitschr. f. Phys.* **41**, (1927), p. 443.

from the standpoint of wave mechanics, and deduced that an atom when struck by a light wave must, under certain circumstances, emit a material wave which is to be regarded, in the sense of Born, as a stream of photo-electrons. The theory developed by Wentzel and by Beck gives the well-known Einstein law * for the velocity of the electrons, and gives results which are well corroborated by experiment for the spatial distribution.

Very recently two very wide and significant fields of application have been opened to the quantum theory by wave and quantum mechanics. These fields, which remained quite untouched by the older quantum theory, concern the problems of molecular compounds and the structure of atomic nuclei. Heitler and London † succeeded, in 1927, in showing on the basis of wave mechanics that the homopolar compounds ‡ of two like atoms, so difficult to explain on the older theory, are the result of resonance phenomena which must occur in the material waves on account of the equality of the electrons. On the basis of this assumption, Heitler and London were able to calculate the energy of combination of the diatomic hydrogen molecule in agreement with the empirical value, and also to show that, in the case of two helium atoms in the normal state, mutual attraction is prevented by Pauli's principle, so that the chemical passivity of helium is thus explained.

These conclusions were later extended by London § to other atoms. London starts from the fact that each state of an atom is characterised by the multiplicity of the system of terms to which the state in question belongs;

* According to this law, the sum of the kinetic energy of the photo-electron and the work done in detaching it is equal to the product of the frequency of the light acting and the elementary quantum of action.

† W. Heitler and F. London, *Zeitschr. f. Phys.* **44**, (1927), p. 458.

‡ Combination between two neutral atoms is known as homopolar, while by heteropolar is meant a combination between two oppositely charged ions. H_2 is a typical example of homopolar, and HCl of heteropolar combination.

§ F. London, *Zeitschr. f. Phys.*, **46**, (1928), p. 455.

thus, for example, in the case of a triplet-term system, the multiplicity is to be taken as three, and so on. Now, according to London, this multiplicity determines the nature of the symmetry of the wave process which must be ascribed to the atom in Schrödinger's configuration space. In this way he arrived at the conclusion that the homopolar valency must be one less than the multiplicity.* In agreement with chemical experience, he finds that the halogens must be mono-, tri-, penta- and heptavalent in their homopolar compounds, with the single exception of the lowest member, fluorine, which appears in London's theory as only monovalent, and which also in actual fact never exhibits a greater valency than this. For the elements of the oxygen group London calculates that, with the exception of oxygen itself, which can only be divalent, they may be di-, tetra- and hexavalent, again in agreement with fact.

A remarkable connection between a phenomenon of optical spectra and one of the problems of nucleus structure has recently been discovered by Heisenberg.† In the band spectra of molecules with identical nuclei, an intensity change occurs which it was formerly attempted to explain by the introduction of quarter quantum numbers. Heisenberg found that the phenomenon is due to a resonance effect in the nucleus ; investigation of the band spectra can therefore lead to conclusions as to the structure of the nucleus. Heisenberg considered that the available experimental material showed that the hydrogen nuclei (*i.e.*, the protons) have a spin, while such a spin is not possessed by the nuclei of helium and carbon, since in these nuclei the resultant of the angular momentum of the protons and electrons composing them vanishes.

* The homopolar valency is equal to the resultant angular momentum of the spin of the electrons, when this angular momentum is measured in units of $\hbar/4\pi$. The resultant angular momentum diminishes by one unit during the saturation of a valency. The homopolar valencies are saturated when the resultant angular momentum of the electrons vanishes.

† W. Heisenberg, *Zeitschr. f. Phys.* **41**, (1927), p. 239.

Finally, Beck * has succeeded in showing that the nuclear structure must be determined by Pauli's principle. He arranged the isotopes, on the basis of the well-known measurements of Aston, in a schéme for which he deduced simple regularities. These regularities, which give a starting point for the building up of nuclear structure, arise, according to Beck, from Pauli's principle, and are due to the spin of the electrons.

* Beck, *Zeitschr. f. Phys.*, **47**, (1928), p. 407.

CHAPTER XVI

QUANTUM MECHANICS AND PHILOSOPHY

THE revolution which has been brought about in physics by the wave theory and quantum mechanics is of so fundamental a character that it is bound, sooner or later, to exert far-reaching influence on the whole of philosophy. The new physical theories open up the possibility of an essential transformation in many of the fundamental conceptions of philosophy, and in none more especially than in the ideas of matter, causality and natural law.

At the end of the nineteenth century the resolution of matter into discrete elementary particles, postulated by the philosophy of the ancients, had been brought to certainty by modern experimental physics. The most recent development of physics has meanwhile imposed essential limitations upon the individual freedom of these particles. At the present time it does not appear possible to give to the elementary particles either a definite localisation or a sharply defined boundary. Each particle influences the others, and, conversely (as is shown by the statistics of Fermi) is affected as to its freedom by them.

The contrast between matter and light (in its widest sense) has been much lessened by the latest development of atomic theory. The essential peculiarities of matter, especially its discontinuity and its property of possessing momentum, are found also in the case of light ; and conversely the undulatory nature of light is found in matter. The corpuscular and undulatory conceptions appear in the physics of to-day, no longer as fundamentally different branches of the science, but as complementary features in a general and universal view of nature.*

* This idea is developed in a particularly clear manner by Bohr in a

In contrast to the sharply defined causality which is evident in macroscopic physics, the latest theories have emphasised the indeterminate nature of atomic processes ; they assume that the only determinate magnitudes are the statistical magnitudes which result from the individual elementary processes of physics. Such a conception naturally opens new perspectives in the problem of physical regularity as such.* A question which continually claims the centre of philosophical interest is that of whether there is in Nature any other kind of regularity than the purely statistical which, on account of its generality, might be common to physics and to other branches of knowledge, such as national economy, for example.†

A glance at the history of theoretical physics suggests as the essence of physical advance the progressive emancipation of physics from the purely human viewpoint. In this sense, the years which have seen the development of the work of de Broglie, Schrödinger and Heisenberg may well be regarded as a period of clarification, which has contributed much to the overcoming of established prejudices.

paper given in September, 1927, before the International Congress of Physics at Como. (See *Nature*, 121, (1928), p. 579.)

* See P. Jordan, "Kausalität und Statistik in der modernen Physik," *Naturwissenschaften*, 15, (1927), p. 205 (also *Nature*, 119, (1927), p. 566). Also, M. Planck, "Physikalische Gesetzmäßigkeit im Lichte neuerer Forschung," *Naturwissenschaften*, 14, (1926), p. 249.

† Experiments on the Compton effect seem to argue against the complete exclusion of non-statistical regularities, since from the experiments the conclusion may be drawn that the laws of conservation of energy and momentum are also obeyed during the collision of a single light quantum with an electron.

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